ABSTRACT

Title of Document: REEVALUATING THE CERCLA PROCESS: A CASE STUDY AT BEAVERDAM ROAD LANDFILL

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This case study consists of a reassessment of the decision making process and chosen remedial action for the Beaverdam Road Landfill (BDRLF) Superfund site. Analyses incorporate case study review, site data, and experimental results to assess whether the chosen remedial action meets the USEPA goals of protecting human health and the environment. The case study evaluation produced conclusions used to assess the chosen remedial action. For site analysis, I reassessed the original data interpretation using pertinent soil gas, soil, surface water, and groundwater data. Experimental work consisted of a batch experiment testing the ability of various biowall media and amendments to degrade TCE relative to site soil and a negative control. I concluded that although CERCLA was generally followed, absence of clear remedial goals and limited interpretation of site data resulted in a remedial action which does not meet the USEPA's goal of protecting human health and the environment.

REEVALUATING THE CERCLA PROCESS: A CASE STUDY AT BEAVERDAM ROAD LANDFILL

By
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Dedication

I dedicate this work to the Great Spirit

Acknowledgements

I would like to thank my advisors for their support over the last two years. Thanks must also be given to BMT Entech for the data they provided. Most importantly, I would like to thank the friends and family who offered their ears and minds to me while I devised this thesis.

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List of Abbreviations

AOC	Area of Concern
ARS	Agricultural Research Service
ATSDR	Agency for Toxic Substances and Disease Registry
BARC	Beltsville Agricultural Research Center
BDRLF	Beaverdam Road Landfill
bgs	Below Ground Surface
CAH	Chlorinated Aliphatic Hydrocarbon
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
COC	Contaminant of Concern
1,2-DCP	1,2-Dichloropropane
DCA	Dichloroethane
DCE	Dichloroethylene
DNAPL	Dense Aqueous Phase Liquid
DO	Dissolved Oxygen
FS	Feasibility Study
HI	Hazard Index
HQ	Hazard Quotient
ILCR	Incremental Lifetime Cancer Risk
K_d	Solid Partitioning Coefficient
K_{oc}	Organic Carbon Partitioning Coefficient
K_{ow}	Octanol Water Partitioning Coefficient
MCL	Maximum Contaminant Level
MNA	Monitored Natural Attenuation
MW	Monitoring Well
NA	Natural Attenuation
NPDES	National Pollutant Discharge Elimination System
NPL	National Priorities List
ORP	Oxidation Reduction Potential
1,1,1,2,2-PCA	1,1,2,2-Perchloroethane
PCE	Perchloroethylene
PID	Photoionization Detector
PP	Proposed Plan
PRB	Permeable Reactive Barrier
QA	Quality Assurance
QC	Quality Control
RBC	Risk Based Concentration
RI	Remedial Investigation
ROD	Record of Decision
SSP	Site Screening Process Site Screening

TAL	Target Analyte List
TCE	Trichloroethylene
TCL	Target Contaminant List
USDA	United States Department of Agriculture
USEPA	United States Environmental Protection Agency
VOC	Volatile Organic Compound

Chapter 1: Introduction

1.1 Site Background

Beaverdam Road Landfill (BDRLF) is located on the north bank of the Beaverdam Creek stream valley in Beltsville, Maryland. USDA actively used BDRLF as a disposal site for non-hazardous substances such as construction rubble and furniture from the early 1940s through the 1980s, after which the landfill was closed and capped with clay. As part of a facility wide Preliminary Assessment/Site Investigation conducted in 1991, USEPA designated BDRLF as an area of concern (AOC). In 1994, USEPA placed the Beltsville Agricultural Research Center on the National Priorities List (NPL) subjecting the BDRLF site to the Superfund or Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA).

Subsequently, several environmental assessments of the site have occurred, including a field reconnaissance study (1996), baseline groundwater sampling (1997), and a Site Screening Process (SSP) investigation (1999). This work identified trichloroethylene, along with a number of other chlorinated solvents at lower concentrations in the shallow groundwater at the site. In accordance with the EPA Superfund process, this prompted a more comprehensive set of site analyses starting in 2002, known as a remedial investigation (RI) and feasibility study (FS). The RI/FS identified the types, quantities, and locations of contaminants and suggested engineered solutions to the contamination. According to the consulting report, the biowall approach was chosen among a number of remedial alternatives due to its perceived relatively low cost, feasible implementation, and presumed effectiveness.

1.2 Site Description

1.2.1 Surface Features

The BDRLF is located on the Beltsville Agricultural Research Facility approximately 1,700 feet east of the intersection of Beaverdam Road and Research Road, on the north bank of the Beaverdam Creek stream valley. The site is a large dome shaped (geotextile capped and soil and vegetative covered) landfill with steeply sloped sides, and is surrounded by woods to the east and south and a cultivated field to the west. The landfill is approximately 500 feet north of Beaverdam Creek and its floodplain. Located within the wooded tract is an unnamed intermittent creek to the east of the landfill that eventually drains into Beaverdam Creek to the south. There are no drainage courses or culverts that lead directly from the landfill to either Beaverdam Creek or the unnamed tributary.

Wetlands on the BDRLF are located on the southern and southeastern edges of the landfill. The remainder of the site consists of filled uplands. The area to the east of the landfill is characterized as transitional with the wetland boundary generally following the topographical contour of the area as shown in Figure 1.

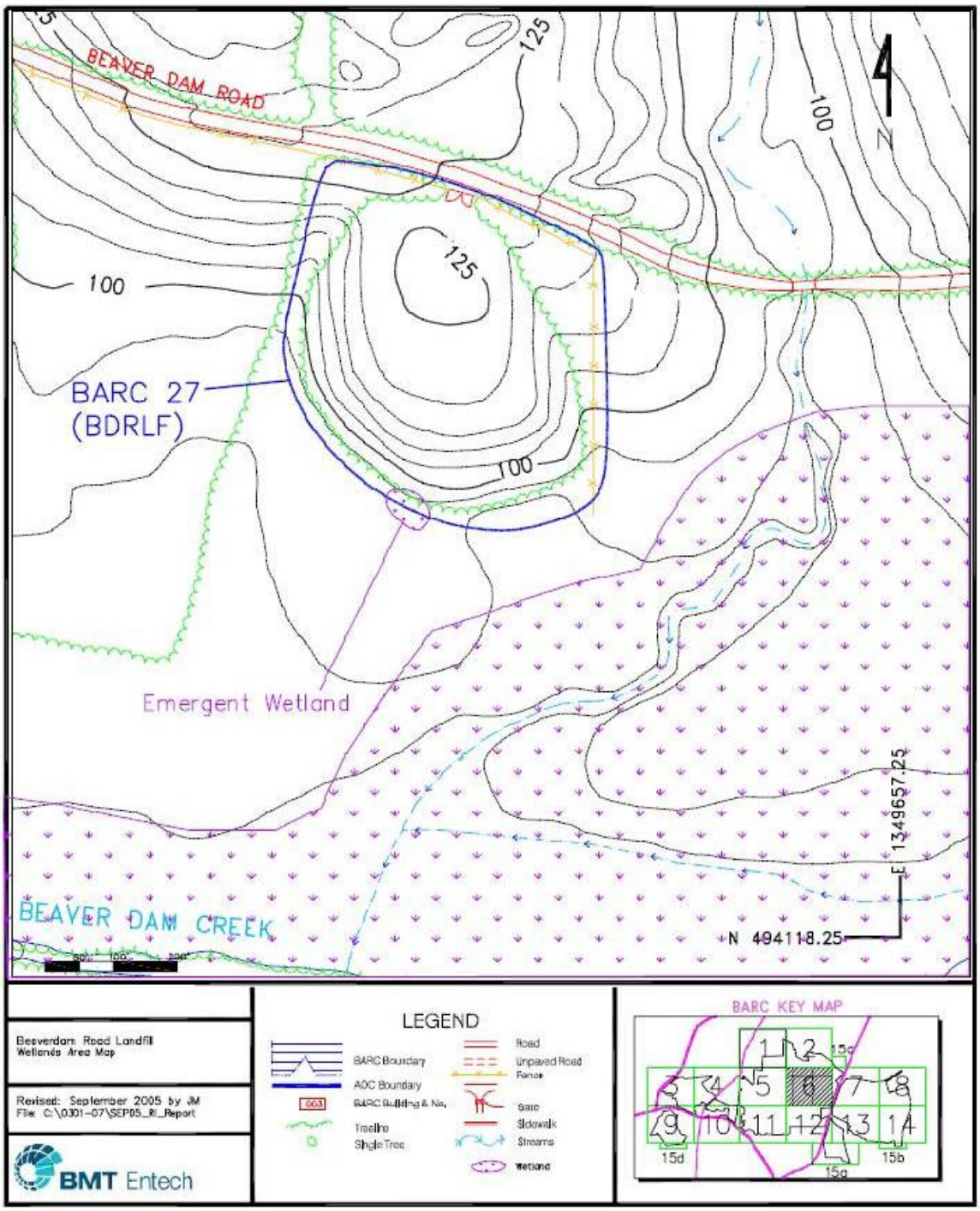

Figure 1 Wetland boundary at BDRLF as defined by BMT Entech.

1.2.2 Geology and Soil

The landfill is directly underlain by the lower Cretaceous Arundel Clay Formation. The soils at the base of the landfill have 20 to 30 feet of alluvial sediment

overlying the Arundel Clay owing to the migration of the creek and its floodplain over time. Groundwater contamination is confined to the alluvial silts, sands, and gravels above the relatively impermeable Arundel Clay.

1.2.3 Hydrology

Groundwater velocities are known to vary at the site. In April of 2010, hydraulic conductivity was measured in monitoring well 2 (MW2) and MW6. Rising and falling slug tests were performed on MW6, but only the falling head test on MW2 because the well recharge levels were excessively slow. Slug tests were analyzed using Hvorslev method by BMT Entech. The resulting hydraulic conductivity values ranged from $6.88x10^{-6}$ cm s^{-1} in MW2 to $1.02x10^{-4}$ cm s^{-1} in MW6 as shown in Table 1. Due to the long duration of the falling head test (8 hours) for MW2 the hydraulic conductivity is considered an over estimate. The differences in hydraulic conductivity between the two monitoring wells may be explained by the soil lithology of the respective areas. In the vicinity of MW2, the soil was compact silt and clay whereas around MW6 the soil consisted of more silts and sands.

Table 1 Slug test summary

	MW-2 (rising head)	MW-2 (falling head)	MW-6 (rising head)	MW-6 (falling head)
Hydraulic conductivity (cm s^{-1})	NA	$6.88x10^{-6}$	$1.02x10^{-4}$	$9.14x10^{-5}$

During baseline groundwater sampling in 1997, BMT Entech assessed the hydraulic gradient and flow direction using static water levels, along with surveyed well locations and elevation data. The hydraulic gradient was determined to be 0.011 and the

flow direction was determined to be south from the landfill. During the remedial investigation the hydraulic gradient was recalculated by measuring water level in the nine monitoring wells, five of which BMT Entech established for the RI. The gradient was found to be 0.0125 and the localized groundwater flow direction was determined to be south-southeast as shown in Figure 2.

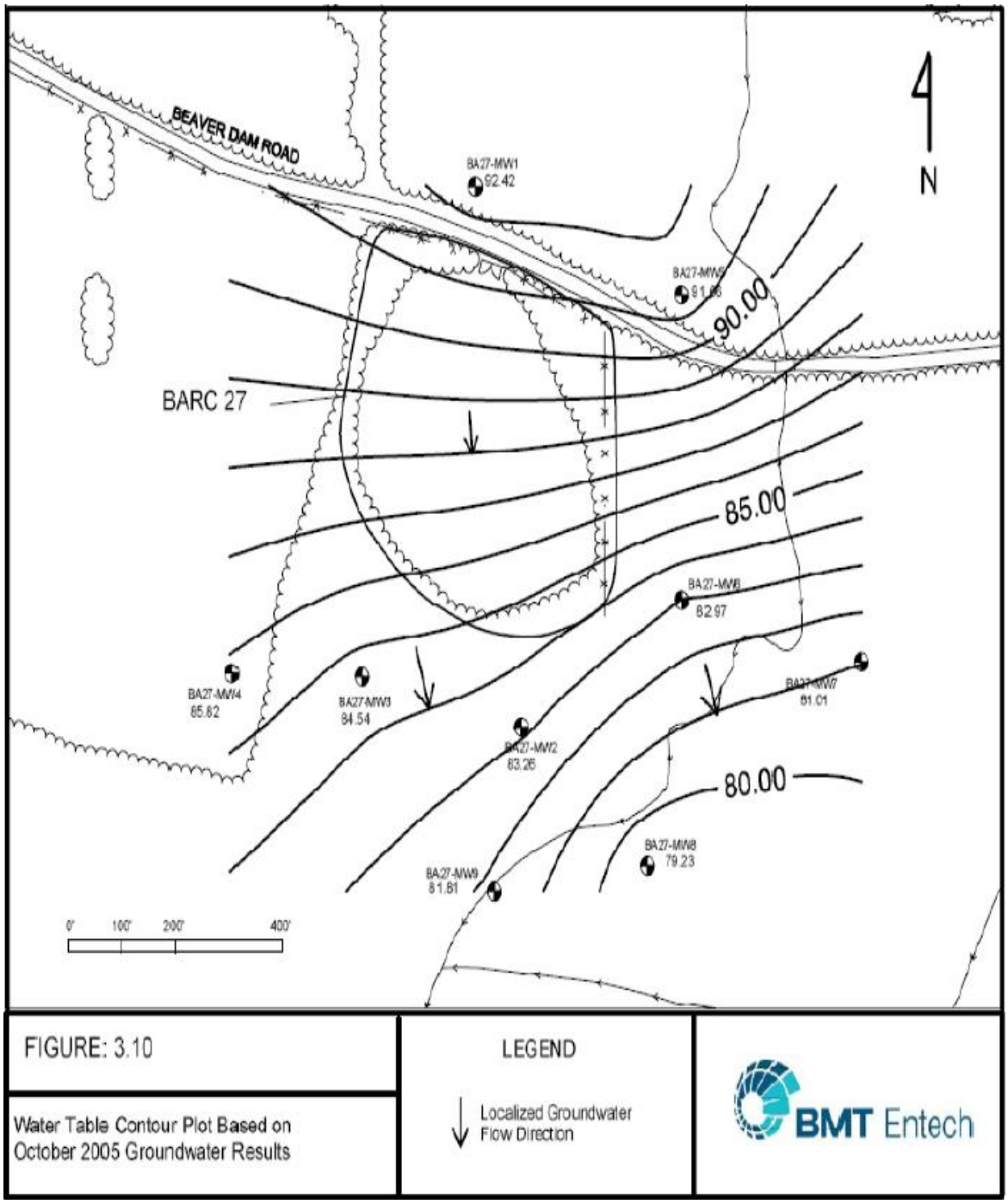

Figure 2 Groundwater flow direction diagram taken from the remedial investigation for BDRLF (BMT Entech 2008b).

BMT Entech originally found the seepage velocity at the site to be 3.16 m yr^{-1} based on an estimated hydraulic conductivity of $1.0x10^{-4}$ cm s^{-1}, measured hydraulic gradient of 0.011, and estimated porosity of 0.3. Using the measured hydraulic

conductivities from 2010 and re-measured hydraulic gradient, the revised seepage velocity for the site ranges from 0.09 m yr^{-1} to 1.34 m yr^{-1}. These data are shown in Table 2 along with the actual expected flow rate of TCE given a retardation factor of 2.

Table 2 Seepage velocity and actual TCE velocity calculation

Monitoring well	Hydraulic conductivity (cm s^{-1})	Hydraulic conductivity (m yr^{-1})	Hydraulic gradient	Seepage velocity (m yr^{-1})	Actual TCE velocity (m mo^{-1})
2	0.00000688	2.2	0.0125	0.09	0.045
6 (rising head)	0.000102	32.2	0.0125	1.34	0.67
6 (falling head)	0.0000914	28.8	0.0125	1.20	0.6

1.3 Site History

Time Line

1943 through 1985- Landfill operated by USDA for disposal of construction rubble, furniture, and other debris.

1980-Landfill access restricted though some disposal continued.

1985- Industrial Waste Management Permit issued by Maryland requiring installation of four monitoring wells and annual sampling.

1991- Post Closure Care and Monitoring Plan

1991- Preliminary Assessment/Site Investigation conducted by APEX consulting firm. Identified the function of the landfill, duration of use, and assessed the potential for release of hazardous substances in the future. The potential was considered low so no groundwater data was collected.

1994- Beltsville Agricultural Research Center (BARC) added to National Priorities List (NPL). The Agricultural Research Service (ARS) agreed to address all areas of environmental concern at BARC pursuant to an executed Federal Facilities Agreement

(FFA) under the Federal Facilities Compliance Act (FFCA). Agreement obligated ARS to investigate and remediate sites in accordance with the National Contingency Plan (NCP), the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), Superfund Amendments and Reauthorization Act (SARA), and other applicable Federal and State regulations.

1996- Field reconnaissance by BMT Entech. Survey of the site revealed debris just east of the landfill within the landfill perimeter fence. Debris included empty 55-gallon drums and a large compressed gas cylinder. The drums were located approximately 100 feet east of the base of the landfill. One of the drums was labeled "10W30 motor oil"; the two drums were identified as "300 Super Premium Engine Oil".

1997- Baseline groundwater sampling of four existing BARC wells by BMT Entech found low levels of TCE (64 µg L^{-1}) and *cis*-1,2-dichloroethylene (12 µg L^{-1}) in MW2. The data gathered were used to assess the existing groundwater condition, flow patterns, and hydraulic characteristics. This is the first available source of groundwater and soils data. Though some data were collected in 1990 by Kidde Consultants, it has not been retrieved. BMT Entech calculated a hazard index in excess of the 0.5 threshold due to metals, but the incremental lifetime cancer risk was below the 5×10^{-5} threshold. Elevated levels all over BARC were later found to nullify the metals found at BDRLF.

January 1998- BARC Desktop Collection Report including BDRLF. Employee interviews were used to assess the use of the landfill. Several employees specifically stated that no chemical disposal occurred at the landfill, though one stated that it could have been possible.

November 1998- Site Screening Work Plan by BMT Entech suggested further action on this site based on poorly documented historical waste disposal practices.

January 1999- Field activities of Site Screening Process (SSP) conducted. The SSP is the mechanism established by CERCLA for determining if the area of concern (AOC) identified warrants remedial action, further study through Remedial Investigation/Feasibility Study (RI/FS) process, or no further action. BMT Entech Sampled four existing monitoring wells, and nine geoprobe locations, including seven along the perimeter of the landfill and two between existing down-gradient wells and the unnamed tributary to Beaverdam Creek. They also collected co-located surface water and sediment samples from five locations, two in the wetland at the base of the landfill and three in the unnamed creek. This study provides the second source of groundwater and soils data.

2002-2008 Remedial Investigation

January 2004- Five additional monitoring wells installed and sampled. At this time, BMT Entech also sampled 20 geoprobe locations. The third available source of data.

August 2004- Monitoring well sampling event 4.

February 2005- Monitoring well sampling event 5.

October 2005- Groundwater analyses including flow direction analysis.

November 2005- Monitoring well sampling event 6.

September 2006- Monitoring well sampling event 7.

March 2006- Draft RI Report submitted to USEPA.

July 2007- USEPA comments received.

March 2008- Final RI Report completed.

April 2008- Monitoring well sampling event 8.

July 2008- Feasibility Study submitted to USDA.

March 2009- Monitoring well sampling event 9.

December 2010- Monitoring well sampling event. No TCE was observed in MW6.

Monitoring well event 10.

March 2011- BMT Entech which had changed its name to BMT Designers and Planners conducted sampling because no TCE had been found in the December sampling of MW6. Plus, they conducted slug tests to measure hydraulic conductivity in MW2 and MW6, relying previously on estimates based on soil type. The other objectives of this field effort included collection of further data on whether TCE is still being released from the landfill and evaluation of the extent to which TCE was being released to the unnamed stream. BMT collected and analyzed geoprobe groundwater samples from seven wells along the extent of the proposed biowall, two around MW6, and one due east of the landfill. In addition, four water samples were collected showing decreased concentrations from the 2004 sampling and still below drinking water standards for TCE.

May 2012- Monitoring well sampling event 11.

Present- In June 2012, SCS engineers finished clearing the approximately 2 acres needed to allow machine access for biowall construction. The next stage of biowall construction awaits funding.

1.4 TCE Background

Trichloroethylene (TCE), perchloroethylene (PCE), and trichloroethane (TCA) are the most frequently detected volatile organic chemicals (VOCs) in ground water in the United States (Fischer, Rowan and Spalding 1987). TCE, the focus of this study, is associated with a number of adverse health effects including neurotoxicity, immunotoxicity, developmental toxicity, liver toxicity, kidney toxicity, endocrine effects, and several forms of cancer. The carcinogenicity of TCE is complex, involving multiple carcinogenic metabolites acting through multiple metabolic pathways. According to the USEPA's cancer guidelines, TCE is highly likely to produce cancer in humans (USEPA 2001).

The unique properties and solvency of TCE have prompted its wide usage as an ingredient in industrial cleaning solutions and as a "universal" degreasing agent (Russel, Matthews and Sewell 1992). TCE is currently used primarily for its solvency of grease to clean fabricated metal parts (USEPA 2011a). It is also commonly used in textile processing, refrigeration, lubricants and adhesives, along with the production of vinyl chloride, pharmaceuticals, and insecticides (Pant and Pant 2009). TCE enters the atmosphere through volatilization during vapor degreasing operations and enters the subsurface as a consequence of illicit or accidental discharge. TCE may also enter surface waters via direct discharge and groundwater releases from contaminated sites (USEPA 2009).

The USEPA drinking water standard for TCE is 5.0 µg L^{-1}. The USEPA has not set a TCE standard for air, but the Occupational Safety and Health Administration (OSHA) has set an exposure limit of 100 mg L^{-1} as the highest permissible level of

exposure averaged over an 8-hour workday. OSHA has set a 5-minute maximum exposure concentration of 300 mg L^{-1} in any 2 hour period (ATSDR 2011b). The four primary daughter products of TCE dechlorination are also regulated under the USEPA. These include 1,1-Dichloroethylene (1,1-DCE), *cis*-1,2-DCE, *trans*-1,2-DCE, and vinyl chloride (VC). The DCE species are associated with liver problems while vinyl chloride increases the risk of cancer (USEPA 2011a). Figure 3 displays TCE and the intermediate chlorinated ethenes associated with it.

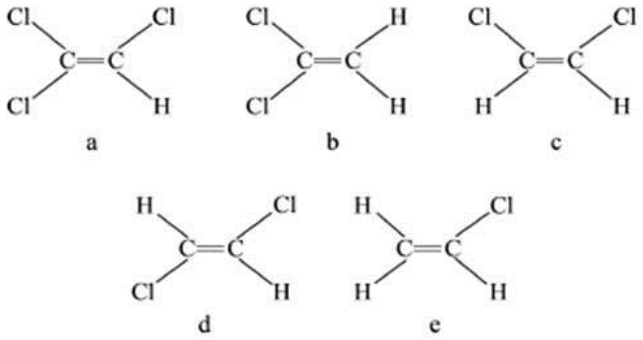

Figure 3 TCE and daughter product molecular structures (a) TCE with three chlorine atoms and one hydrogen atom bonded to carbon atoms; (b) 1, 1-DCE; (c) cis^{-1},2-DCE; (d) trans^{-1},2-DCE; (e) vinyl chloride (Adapted from Pant and Pant, 2009).

1.4.1 Factors Affecting TCE and Daughter Product Groundwater Transport

1.4.1.1 Hydgrogeologic Considerations

There are four key hydrogeologic parameters that affect the transport of TCE and related compounds in the groundwater. These include seepage velocity (Vs), hydraulic conductivity (K), hydraulic gradient (i), and effective porosity (n). Seepage velocity expressed in units of length per time (e.g. ft yr^{-1}) is the actual interstitial ground-water velocity, equaling Darcy velocity divided by effective porosity. Typical values are 0.5 to 200 ft yr^{-1} (Aziz et al. 2000). This parameter is calculated by multiplying the hydraulic conductivity by hydraulic gradient and dividing by effective porosity.

The effective porosity is a dimensionless ratio of the volume of interconnected voids to the bulk volume of the aquifer matrix. It differs from "total porosity" in that it excludes all non-connected pores. This parameter is usually estimated. For example, one commonly used value for silts and sands is an effective porosity of 0.25. Domenico and Schwartz (1990) report a range of effective porosity values for different soil textures. These data are summarized in Table 3.

Table 3 Porosity for different soil textures

Soil Texture	n (unitless)
Clay	0.01-0.20
Silt	0.01-0.30
Fine Sand	0.10-0.30
Medium Sand	0.15-0.30
Coarse Sand	0.20-0.35
Gravel	0.10-0.35
Sandstone	0.005-0.10
Unfract. Limestone	0.001-0.05
Fractured Granite	0.00005-0.01

*Domenico and Schwartz, 1990

Hydraulic conductivity describes the rate at which water can move through a permeable medium. The density and kinematic viscosity of the water must be considered when determining hydraulic conductivity (Fetter 2001). Pump tests or slug test are used to measure hydraulic conductivity. Typical values for K for a range of soil textures are displayed in Table 4. Hydraulic gradient refers to the slope of the potentiometric surface, which in unconfined aquifers amounts to the slope of the water table. This parameter is expressed in units of length per length. Typical values fall in the range of 0.0001 – 0.05 ft ft^{-1}.

Table 4 Values for hydraulic conductivity (K)

Soil Texture	K (cm s^{-1})
Clays	$<1x10^{-6}$
Silts	$1x10^{-6}$ - $1x10^{-3}$
Silty sands	$1x10^{-5}$ - $1x10^{-1}$
Clean sands	$1x10^{-3}$ – 1
Gravels	> 1

1.4.1.2 Dispersivity

Dispersion refers to the process whereby a dissolved solvent will be spatially distributed longitudinally, transversely, and vertically because of mechanical mixing and chemical diffusion in the aquifer. Combined, these processes result in the plume shape characteristic of dissolved solvent masses in an aquifer. Field measurement of dispersivity is difficult; however, estimations may be made based on the length of the plume or distance to the measurement point. Dispersivity values can range over 2-3 orders of magnitude for a specified plume length or distance to measurement point (Gelhar, Welty and Rehfeldt 1992).

1.4.1.3 Physio-chemical properties of TCE and related daughter products

The most relevant physio-chemical properties of TCE and related chlorinated ethenes at 25°C and 1 atm are presented in Table 5. For use of the presented dimensionless Henry's constants at different temperatures, one must use the van't Hoff equation to make adjustments (Schwarzenbach, Gschwend and Imboden 2003).

Table 5 Physio-chemical properties of TCE and daughter products at STP

Compound	Molecular Weight[a]	H[b] (dimensionless C_a/C_w)	Vapor Pressure[c] (mm Hg)	Solubitlity[c] (mg L^{-1})	Koc[b] (L kg^{-1})
PCE[c]	165.8	1.21	19	143	269.2
TCE	131.4	0.39	58	1000	153.9
cis-DCE	99	0.34	200	800	52.33
trans-DCE	99	0.4	331	600	69.62
1,1 DCE	99	1.62	59.1	5500	74.83
VC	62.5	5.95	266	2540	33.87

[a] (Schwarzenbach et al. 2003)

[b] (Dong et al. 2008)

[c] (Wiedemeier et al. 1999)

The density of TCE is 1.46 g ml^{-1}, which is greater than water's density of 1 g ml^{-1} making it heavier than water. This means that spilled TCE in excess of the compound's water solubility of 1000 mg L^{-1} will sink through the subsurface until low permeability formations stop its movement. In the environment, TCE forms plumes of dense nonaqueous phase liquid (DNAPL) at the base of an aquifer and a trail of residual saturation in the path of downward transport. Pools of TCE DNAPL can serve as source areas for ground water contamination as unsaturated groundwater contacts the pool and TCE partitions into the aqueous phase. For example, at a site in Texas it was determined that 8 kg of non-aqueous phase TCE was responsible for contaminating 12.3 x 10^6 gallons of water at an average concentration of 176 ppb (as cited in Russel et al. 1992)

The Henry's Law Constant is a measure of the tendency of a compound to volatilize once dissolved in water. For TCE, the Henry's Constant is 967 Pa-m^3/mol or 0.39 dimensionless at 20°C (Table 5), which makes for relatively rapid transfer to the atmosphere. As cited by (Russel et al. 1992), the evaporation half-life of TCE in water is on the order of 20 minutes at room temperature in both static and stirred vessels. Henry's constant varies slightly between authors and is directly proportional to temperature.

Also, the dimensionless Henry's constant may be represented as an air-water or water-air parameter. Here, the dimensionless Henry's constant used equals the gaseous TCE concentration (C_a) divided by the aqueous concentration (C_{aq}). Henry's constant will vary with temperature and may be adjusted using the van't Hoff equation, derived empirically at varying temperatures, or calculated using formulations such as that devised by Heron et al. (1998), which is what was done in this report.

1.4.1.4 Adsorption

The K_{oc} can be estimated from the water solubility and octanol water coefficient, but in the case of TCE a number of empirically derived values exist. Chiao et al. (1994), found an average K_{oc} of 86 from 13 literature values. The values considered by Chiao et al. (1994) were derived empirically for a range of soils, organic matter contents, and TCE concentrations. This value is nearly the same as the conservative value of 87 L kg^{-1} reported in the literature (Wiedemeier et al. 1999).

Shen and Wilson (2007) found K_{oc} values using three different methods including a tracer study, 48 hr sorption isotherm study, and a 25 day batch sorption study. The values for each method were 5.3, 21, and 14 L kg^{-1} respectively, though the authors use the highest of the values as a reference in their paper. The media they tested was similar to the media used in this study composed of 50% (v/v) shredded tree mulch, 10% (v/v) cotton gin trash, and 40% (v/v) sand.

The literature contains little information on TCE partitioning to organic rich materials, but Zytner (1992) reported a K_{oc} for peat moss of 189 L kg^{-1}, a K_{oc} for organic rich top soil of 115 L kg^{-1}, and a K_{oc} for sandy loam soil of 50 L kg^{-1}. Shen and Wilson attribute the low values they found to a lower surface area to volume ratio in the plant

mulch used, but do not make any measurements to test their conjecture. Dong et al. (2009) use a value of 159 L kg^{-1} falling on the high end of those reported by Chiao et al. Dong et al. provide values for the entire group of chlorinated ethenes related to TCE, making this paper a valuable reference. The values for K_{oc} displayed in Table 5 come from this paper. Regardless of the K_{oc} value used for reference, the wide variability in literature values indicates the need to establish specific organic partitioning coefficient values for the media under question.

The distribution coefficient (K_d) represents the mass of some constituent, such as TCE, per unit mass of soil divided by the mass of the constituent per unit volume of water in contact with the soil. For TCE in the ground-water zone, K_d can be estimated using the relation $K_d = K_{oc} \times f_{oc}$ where f_{oc} equals the fraction of organic carbon in the ground water zone. This parameter is site specific and depends on the fraction of organic carbon in the ground-water zone and on the value of K_{oc} (Chiao, Currie and McKone 1994).

The retardation factor is a function of adsorption defined as the ratio of the ground-water seepage velocity to the rate that organic chemicals migrate in the ground water. A value of 2 indicates that if the ground-water seepage velocity is 100 ft yr^{-1}, then the organic chemicals migrate at approximately 25 ft yr^{-1}. Values typical for solvents in shallow aquifers are 1 to 6. The actual value is usually estimated using soil bulk density (ρ_b), effective porosity (n), and the distribution coefficient (K_d) as shown in Equation 1:

(Eq. 1) $$R=1+K_d\rho_b/n$$

A range of values for the retardation factor of TCE have been reported depending on the type of aquifer and concentration of TCE studied. If the retardation factor is

assumed to be 2 based on the work of Mehran, Olsen and Rector(1987), then TCE should move at half the speed as water through soils and aquifers.

1.4.2 Distribution of trichloroethylene in the environment

Based on the chemical and physical properties of TCE, one would expect to find the contaminant distributed throughout the environment in the air, ground and vadose water, and for short periods in surface water. Indeed, (Cohen and Ryan 1985) used an estimate made by the USEPA and others that 60% of the total TCE produced in the United States is lost to the atmosphere, with negligible discharge into water bodies. The subsurface environment has experienced significant contamination with TCE in both the vadose and saturated zones. This problem stems from spills, leaking transfer lines, storage tanks and poor environmental awareness. Once in the subsurface, the high density and low K_{oc} of TCE encourages downward movement into groundwater until an impermeable barrier is reached. When a spill is of a large enough volume or deep enough in the ground, losses to volatilization may be insignificant compared to transport in groundwater (Russel et al. 1992).

In the vadose zone, TCE may enter the aqueous phase via soil pore water, the gas phase via volatilization, or exist as NAPL. The ability to exist in each of these three phases highlights the potential upward or downward mobility of TCE in the subsurface. Although large spills may move rapidly through the vadose zone and into groundwater until an impermeable layer is reached, smaller spills are restricted by the surface tension exerted at the capillary fringe of the water table. Once a DNAPL plume of TCE reaches an impermeable layer the flow of the contaminant will coincide with groundwater flow and follow the horizontal orientation of the impermeable layers. TCE existing as

DNAPL at the top of an aquitard will contribute TCE to solution as groundwater flows over and around it, thereby accelerating the spread of the contaminant.

1.4.3 Degradation mechanisms and coefficients

Chlorinated aliphatic hydrocarbons (CAHs) may be degraded via three metabolic processes. Reductive dechlorination is an anaerobic process in which chlorinated ethenes are used as electron acceptors. Co-metabolism is an aerobic process in which chlorinated ethenes are degraded as a result of fortuitous biochemical interactions which yield no benefit to the bacteria. Direct oxidation is an aerobic or mildly anaerobic (iron reducing) process in which minimally chlorinated ethenes are used as electron donors. At a given site, one or all of these processes may contribute to TCE degradation (Byl and Williams 2000).

Reductive dechlorination, the main degrading process believed to occur in biowalls and other permeable reactive barriers, occurs under anaerobic conditions, yielding ethene or ethane as final products as shown in Figure 4. At each reaction step, a chlorine atom is replaced by a hydrogen atom, producing hydrochloric acid (HCl) as a byproduct. Among the environmental conditions that determine the effectiveness of reductive dechlorination, the most important may be the concentration of other organics to act as electron donors. Also, other electron acceptors can hinder TCE dechlorination. These electron acceptors are oxygen, nitrate/insoluble manganese, insoluble ferric iron, sulfate, and carbon dioxide, in order of bacterial preference (Pant and Pant 2009). Reductive dechlorination is the process assumed to play the most significant role in TCE degradation in biowalls.

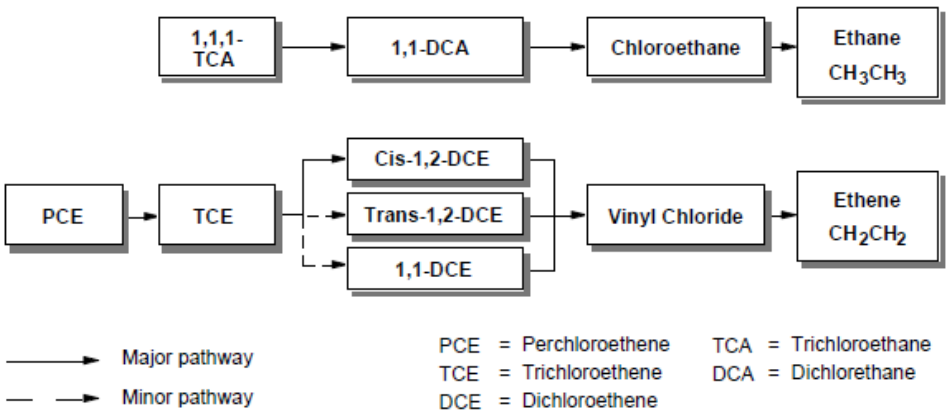

Figure 4 Reduction dechlorination pathways for common CAHs (Vogel and McCarty 1985, Vogel and McCarty 1987).

In addition to microbially mediated reductive dechlorination, TCE and the other CAHs may be reduced by reactive metal-sulfide minerals (e.g. iron-monosulfide). When the process results from biological and geochemical processes, it is referred to as in situ biogeochemical transformation. There are two pathways for abiotic degradation of TCE by FeS (Butler and Hayes 2001). The most important pathway accounting for 80-90% of degradation at pH 7.3, produces acetylene. Bacteria readily ferment acetylene to ethanol and acetate, which sulfate or iron (III) reducing bacteria readily oxidize to carbon dioxide (Kennedy et al. 2006). The other abiotic pathway produces *cis*-DCE, which may also experience anaerobic biological oxidation to carbon dioxide (Bradley 2003). Dong et al. (2008) found that abiotic transformation of PCE and TCE in a microcosm study was typically much slower than microbial reductive dechlorination. This difference in degradation rates was attributed to the slow abiotic transformation of PCE and TCE by reactive minerals that were present at concentrations typically below 1 g/L.

Alternatively, Shen and Wilson (2007) found that abiotic transformation of TCE associated with FeS provided a major contribution to the removal of TCE from the

groundwater at Altus AFB. This was attributable to the high concentrations of sulfate in the groundwater ranging from 1400 to 2600 mg L^{-1}(He, Wilson and Wilkin 2008). Therefore, it is expected that with sufficient sulfate and reactive iron species both abiotic and biotic degradation of TCE could significantly contribute to mass reductions in TCE.

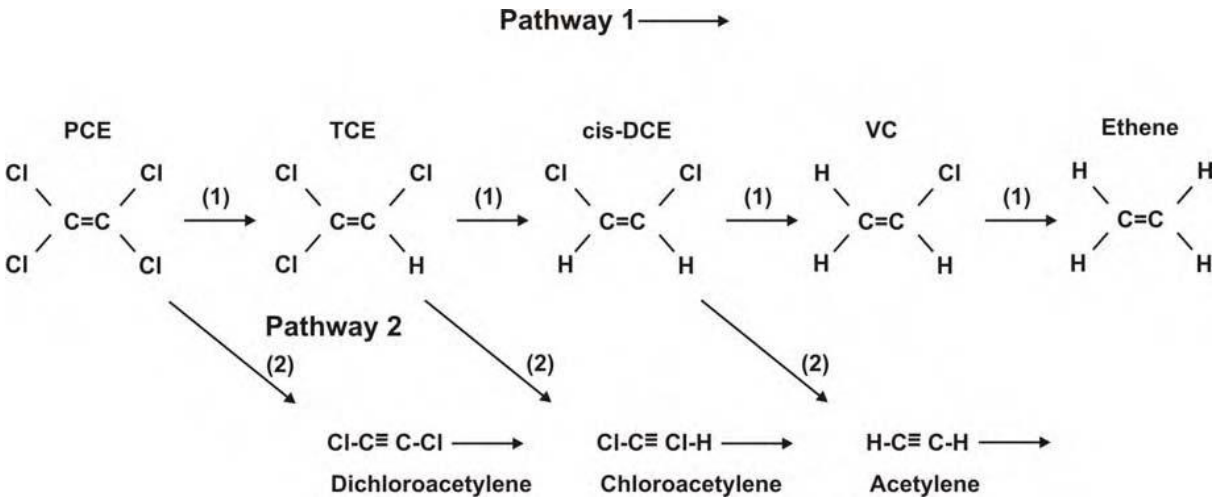

Figure 5 Pathways for (1) biotic reduction of TCE and (2) abiotic reduction by iron monosulfide (modified from Butler and Hayes, 2001).

Co-metabolism of TCE and the other CAHs is carried out by methanotrophic bacteria in soil conditioned with methane. Methane monooxygenase (MMO) is the enzyme responsible for aerobic degradation. This process is termed co-metabolism because the reaction uses enzymes, but does not provide any useable energy to the microorganisms (Alvarez-Cohen and McCarty 1991). This process is illustrated in Figure 6 for TCE degradation.

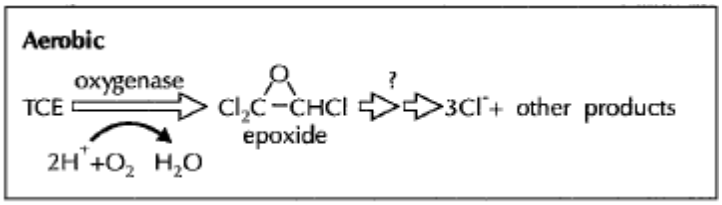

Figure 6 Cometabolism of TCE by methane monooxgenase under aerobic conditions (McCarty 1993).

Direct oxidation of chlorinated solvents involves the less chlorinated reductive dechlorination products acting as electron donors for some bacteria. These bacteria can use VC and DCE as an energy and organic carbon source (Pant and Pant 2009). This process may occur in the presence or absence of oxygen. Bradley et al. (1998a and 1998b) found that humic acids in mulch and compost mixtures may serve as electron acceptors in energy yielding reactions that result in the oxidation of DCE and VC under anaerobic conditions. An example of an energy yielding aerobic VC oxidation pathway is shown in Figure 7.

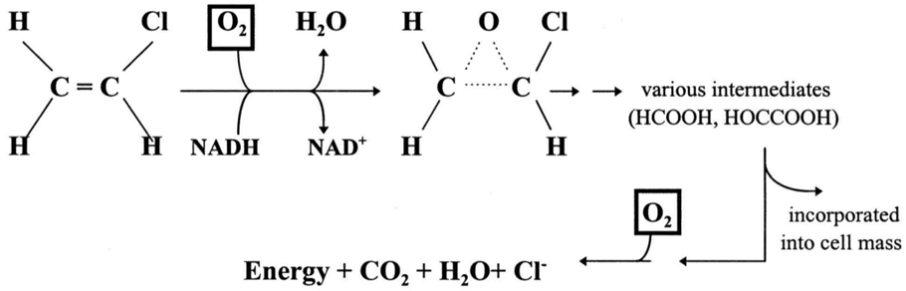

Figure 7 Intracellular VC degradation pathway yielding energy to the organism(Hartmans and De Bont 1992).

TCE degradation has been represented using first-order decay such that the rate of biotransformation depends on the concentration of the contaminant and the rate coefficient (Aziz et al. 2000). When sequential first order decay is occurring, the decay of the solvent in question proceeds via first order kinetics, but it is also simultaneously produced by the preceding compound. Typical value ranges for the most common chlorinated solvents are displayed in Table 6 along with their half-lives (Data adapted from Wiedemeir et al. 1999). The half-life equals 0.693 divided by the first-order decay coefficient.

Table 6 First order biodegradation constant and half-life range for TCE and related chlorinated solvents

Compound	*First order decay coefficient (yr^{-1})	*half-life in groundwater
Perchloroethylene	0.07 to 1.20	9.9 to 0.58
Trichloroethylene	0.05 to 0.9	13.86 to 0.77
cis-1,2-Dichloroethylene	0.18 to 3.3	3.85 to 0.21
Vinyl Chloride	0.12 to 2.6	5.78 to 0.27

*Weidemeier et al. 1999

1.4.4 Modeling Chlorinated Solvent Transport

The fate and transport of TCE in the environment can be modeled using a number of modeling techniques though the USEPA has created two user-friendly models for the task. These are BIOCHLOR and REMchlor or Remediation Evaluation Model for Chlorinated Solvents. BIOCHLOR and REMchlor differ in the analytical method used to model transport and degradation and the underlying assumptions made about the source area. REMChlor can account for variations in groundwater source and plume remediation while the BIOCHLOR assumes a constant source concentration. This allows the user of REMChlor to consider various engineered remediation methods as well as natural attenuation in the source area. Indeed, the main difference between REMChlor and previous models including BIOCHLOR is that the former provides the means to represent chemical reaction parameters (rates, yield coefficients) as functions of both time and distance from the source (Falta 2008). In this section, I provide background on the BIOCHLOR model because I use it to assess the chosen remedial action. A shorter summary of REMChlor is provided for comparison.

BIOCHLOR was developed by a team of researchers supported by the U.S. Air Force Center for Environmental Excellence (AFCEE) to simulate natural attenuation of

chlorinated solvents in groundwater under anaerobic reducing conditions. The model is programmed to run in Microsoft Excel and based on the Domenico analytical solute transport model. BIOCHLOR simulates 1-D advection, 3-D dispersion, linear adsorption, and biotransformation via reductive dechlorination. Three different model types may be tested with the tool including (1) solute transport without decay, (2) solute transport with biotransformation modeled as a sequential first-order decay process, and (3) solute transport with biotransformation modeled as a sequential first-order decay process with two different reaction zones (each zone has a different set of rate coefficients) (Aziz et al. 2000).

BIOCHLOR aims to answer the question, how far will a dissolved chlorinated solvent plume extend if no engineered controls or source area reduction measures are implemented? It does so by predicting the maximum extent of dissolved-phase plume migration, which may then be compared to potential exposure points. BIOCHLOR was intended for two uses. First, as a model to determine whether the potential for natural attenuation is high enough to warrant a thorough natural attenuation study. Secondly, as a remediation by natural attenuation (RNA) ground-water model to address selected chlorinated solvent problems.

BIOCHLOR is limited to applications with simple ground-water flow conditions and should not be used where pumping systems create a complicated flow field or where vertical flow gradients affect contaminant transport. BIOCHLOR simplifies site conditions by assuming constant source, hydrogeological, and biological parameters. Therefore, the model should not be applied where extremely detailed, accurate results are required. BIOCHLOR is limited to use with chlorinated ethanes and ethenes that degrade

via sequential reductive dechlorination and should not be applied to compounds that do not degrade based on sequential first-order kinetics.

Input data categories for the model include hydrogeologic, dispersivity, adsorption, biotransformation, general, source, and field data. Hydrogeologic parameters include seepage velocity (Vs), hydraulic conductivity (K), hydraulic gradient (i), and effective porosity (n). Dispersivity can be represented longitudinally, transversely, and vertically. The user is given some common values for longitudinal dispersivity and relationships for calculation of transverse and vertical. Adsorption data include aquifer matrix bulk density, organic carbon partition coefficient (K_{oc}), fraction organic carbon (f_{oc}), and retardation factor (R), which is a function of the other parameters. Biotransformation is represented with the first-order decay coefficients or dissolved solvent half-lives ($t_{1/2}$) for the compounds of interest. General input parameters include the length and width of the model area and simulation time. Source data include the source contaminant concentrations, width, and depth. Field concentrations and distances from source may be entered to help calibrate the model.

REMChlor is a screening-level mass balance approach for simulating the transient effects of simultaneous ground water source and plume remediation. The modeling tool combines separate models of source and plume behavior to achieve simultaneous consideration of partial source remediation and contaminant degradation within a plume. The contaminant source model is based on a power function relationship between source mass and source discharge. The model serves as a time-dependent mass flux boundary condition to a new analytical plume model, where flow is assumed to be one dimensional, with three-dimensional dispersion. The plume model simulates first-order sequential

decay and production of several species, and the decay rates and parent/daughter yield coefficients are variable functions of time and distance. Using REMChlor one may simulate natural attenuation or remediation efforts that enhance plume degradation. The plume remediation effort may be temporary or delayed in time, limited in space, and it may have different chemical effects on different contaminant species in the decay chain (Falta, 2008).

1.5 Comprehensive Environmental Response Compensation and Liability act (CERCLA) Background

The Comprehensive Environmental Response, Compensation and Liability Act (CERCLA), commonly known as Superfund, was enacted by Congress on December 11, 1980. As the name Superfund suggests, CERCLA created a tax on the chemical and petroleum industries and over five years created a $1.6 billion trust fund for cleaning up abandoned or uncontrolled hazardous waste sites. The law is comprised of three main elements starting with the establishment of prohibitions and requirements concerning closed and abandoned hazardous waste sites. It provided for liability of persons responsible for releases of hazardous waste at these sites; and established a trust fund to provide for cleanup when no responsible party could be identified.

The law authorizes short-term and long-term response actions. Short-term removals occur when actions may be taken to address releases or threatened releases requiring rapid response. Long-term response actions occur in the event of releases or threats of releases of hazardous substances that are serious, but not immediately life threatening. The latter action occurs only if a site is listed on USEPA's National

Priorities List (NPL). Such is the case at BDRLF and the remedial action underway there is a long-term response. CERCLA made the revision of the National Contingency Plan (NCP) possible. The NCP provides the procedures and guidelines used to respond to actual and potential hazardous releases. The NPL was also created from the revised NCP.

In the case of BDRLF, the USDA was the agent responsible for addressing the perceived contamination. As is often the case, USDA hired a consulting firm, BMT Entech, to navigate the CERCLA process. It was thus BMT Entech's job to follow the USEPA stated process until BDRLF could be removed from the NPL. The process starts with discovery of a site, which may be made by citizens, state agencies, the USEPA, or the perpetrator. Then USEPA evaluates the potential for release of hazardous substances from the site through the Superfund cleanup process. First, a Preliminary Assessment/Site Inspection (PA/SI) is made wherein it is assessed whether a site requires immediate or short-term response actions. If the site is deemed a definite threat it is placed on the NPL. Next, the Remedial Investigation/Feasiblity Study (RI/FS) is undertaken. The RI determines the nature and extent of contamination. The FS assesses the treatability of site contamination and evaluation the potential performance and cost of treatment technologies.

The Record of Decision establishes and explains the chosen cleanup alternative. The Remedial Design/Remedial Action comprises the preparation and implementation of plans and specification for applying site remedies. This is when the bulk of cleanup is supposed to occur. Construction Completion identifies completion of physical cleanup construction, but does not indicate whether the cleanup was successful. Post Construction

Completion is meant to ensure that Superfund response actions provide for the long-term protection of human health and the environment. A site is deleted from the NPL once all response actions are complete and all cleanup goals have been achieved. Finally, a site may be reused or redeveloped (USEPA 2011b).

1.6 Scope of Work

This report presents a case study of the remediation process for the Beaverdam Road Landfill (BDRLF), consisting of a reassessment of the decision making process and chosen remedial action. Analyses incorporated literature review, previously collected data, and experimental data to assess whether the process and final decision at BDRLF meet the USEPA goals of protecting human health and the environment. With the case study review, I reevaluated the assumed efficacy of the biowall. In it, I scrutinized the methods and conclusions reached in the several reports and peer-reviewed literature on the topic. The analysis of site data consisted of a review and reevaluation of data collected by BMT Entech between 1997 and 2012. Employing GIS, I made maps showing the temporal and spatial trends in TCE contamination which I used to answer the question underlying the thesis. I also used site data to reevaluate the potential for natural attenuation at the site.

The experimental component was originally conceived exclusively to assist in the design of the biowall, but is now serving the double purpose of providing data to assess the chosen remedial action. We compared ten biowall treatments to degrade and retard chlorinated ethenes. The ten treatments are divided into two baseline mixtures, MX1 and MX2, described volumetrically as (1) 30% mulch, 30% compost, 40% sand and (2) 50% mulch, 10% compost, and 40% sand. Within the first baseline mixture, we assessed the

effects of three doses of zero valent iron 0, 10, 100 ml L^{-1} and three doses of crude glycerol 0, 10, 30 ml L^{-1} of solid. We also examined two combinations of the low and high amendment levels. For MX2, we only tested non-amended mixture, the low dose of ZVI and glycerol, and the combination of the low amendments due to the hypothesis that MX1 would outperform MX2.

To answer whether the biowall meets the USEPA's mission statement, I use the empirical research, site analysis, and literature review to address the following questions: (1) can we prove efficacy of the biowall once it is installed, (2) does the biowall meet the remedial action objectives established in the feasibility study, (3) does the biowall address the assessed risk, (4) and is the risk worth acting on? I provide a separate discussion of the performance of the biowall materials and reassess the potential for natural attenuation at the site, relating both of these sections to the four questions in the conclusion of the thesis. Additionally, I provide a synthesis of my findings and a response to the thesis including recommendations for future application of biowalls and lessons from this case study that can benefit future remedial actions.

Chapter 2:Case Study Evaluation

Mulch biowalls have been installed in at least 13 facilities in 11 states to treat primarily CAHs, but also perchlorate and explosive compounds. In the following case study review, I summarize and critique biowall use at the following sites: Altus Air Force Base (AFB), Oklahoma, Offut AFB, Nebraska, and Seneca Army Depot, New York. These sites were chosen for their similarities in regard to contaminant concentrations and aquifer characteristics, and the amount of information available about the sites. To provide background on the potential effectiveness of permeable reactive barriers at degrading chlorinated ethenes, I summarize the biowall project for each of these sites and then present a critical analysis of biowall performance. Table 7 provides the seepage velocities and TCE flow rates through the aquifer materials at each of the sites and includes the USDA Beaverdam Road Landfill (BDRLF) for comparison.

Table 7 Seepage and TCE flow rates through groundwater

Site	Seepage velocity (m month^{-1})	Retardation factor	TCE velocity (m month^{-1})
Altus AFB	0.86	2	0.43
Offut AFB	7	2	3.5
Seneca Depot	0.43	2	0.21
BDRLF	0.11	2	0.056

2.1 Altus Air Force Base pilot scale biowall

The biowall at Altus AFB was installed at Oklahoma, USA from June 19 to 23, 2002. It was comprised of 228 m^3 (300 yd^3) of mulch (50 % of volume), 46 m^3 (60 yd^3) of cotton gin compost (10% of volume), and 201 m^3 (265 yd^3) of sand (40%). A northerly and southerly transect were installed perpendicular to the biowall to establish

upgradient, within biowall, and downgradient chlorinated ethene concentrations. Sampling of groundwater occurred approximately 8 meters upgradient, within the biowall, and downgradient from the biowall at 1.5, 3, 9, and 29 meters. These transects along with sampling points later installed by the USEPA are shown in Figure 8.

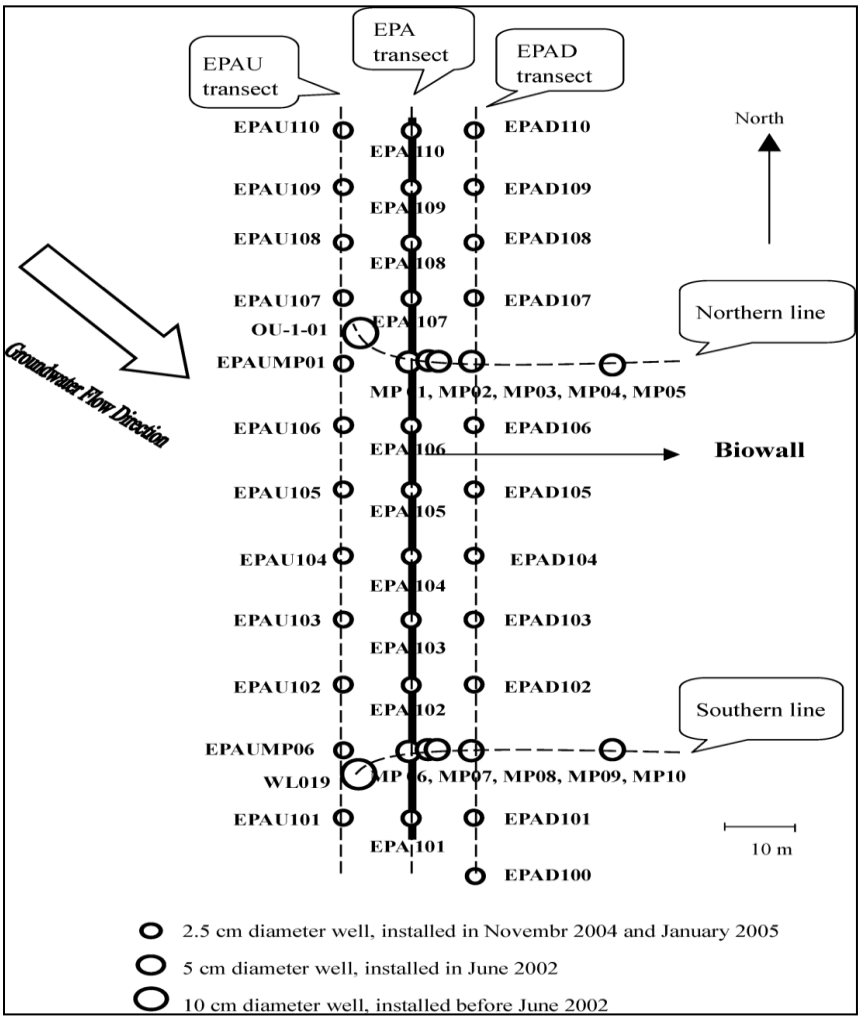

Figure 8 Altus Air Force Base sampling illustration from Lu et al. (2008).

Sampling occurred at 1 month from installation (July 2002), 3 months (September 2002), 9 months (March 2003),17 months (November 2003), 25 months by USEPA (July 2004) (USEPA), 34 months (April 2005), and a partial sampling in April 2007 by the USEPA 58 months after installation. Along the two transects perpendicular to the

biowall the primary contaminants detected at the site were TCE and *cis*-DCE. The highest concentration of TCE measured during monitoring was 8 mg L^{-1} at the northerly upgradient monitoring well. Concentrations of *cis*-DCE ranged up to 1.8 mg L^{-1} at the northerly upgradient monitoring well. Additional monitoring wells (2.5 cm diameter) were installed by the USEPA National Risk Management Research Laboratory/Ground Water and Ecosystems Restoration Division (NRMRL/GWERD) in November 2004 and January 2005 along three transects parallel to the biowall upgradient, within, and downgradient of the biowall. They were subsequently sampled in April 2007, giving a total of 58 months of biowall performance data.

There are a number of problems with the quality of the data reported by (Lu et al. 2008, Henry 2008) including potential errors with the sampling approach. For instance, (Lu et al. 2008) state that water samples were collected with a peristaltic pump at the well head using a polyethylene plastic tube inserted into the well. Pearsall and Eckhardt (1987) found that groundwater samples collected with a peristaltic pump showed significantly lower TCE concentrations than samples collected with a submersible pump as done at BDRLF. The USEPA approved method for measuring volatile organic compounds in groundwater is USEPA Method 5030B. It utilizes 40 mL glass screw-cap volatile organic compound analysis (VOA) vials fitted with Teflon-faced silicone septum caps. The vials must be completely sealed and filled at the time of sampling to prevent air loss and TCE volatilization of the water. They must also be labeled and stored at 4°C. Although the samples were preserved with trisodium phosphate and stored in a cooler, the exact vessel used to store the samples is unknown as is the storage temperature. These

errors were consistent at least and may not as a consequence have affected reported removal efficiencies.

Another issue is that background contaminant concentrations along the transects studied were never established. Although two wells upgradient from the biowall existed and were monitored before 2002, no downgradient wells in line with the eventual North and South transects existed. Therefore, it is erroneously assumed that the entire observed decrease in CAH concentrations downgradient from the biowall is attributable to degradation. The impacts of dilution and dispersion must be accounted for accurate assessments of biowall effectiveness.

Groundwater flow rates and TCE retardation within the groundwater influence the observed TCE concentrations. The authors' calculation of removal efficiency owing to the biowall was flawed by their failure to consider groundwater flow and TCE retardation. The seepage velocity reported by Henry (2008) was 0.1 ft/day. This is equivalent to 36 feet/yr. However, if you assume a minimum retardation factor of 2 (Mehran et al. 1987) in the groundwater and convert to metric, then TCE would have only moved 25 meters after 58 months at 0.43 meters/month.

This means that the reporting of chlorinated ethenes at 29 meters (~100 ft) from the biowall never actually represented TCE that had passed through the biowall from the upgradient well. Moreover, it probably means that all of the measurements at the furthest downgradient monitoring well actually represent background TCE concentrations totally unaffected by the biowall. Table 8 shows the distance between the monitoring wells and biowall-upgradient wells, expected amount of time needed for TCE to reach the monitoring wells, and the sampling times in months from biowall installation. As seen in

Table 8, accurate calculations of removal efficiencies due to the biowall at the given monitoring wells downgradient would require sampling at 10, 12, 19, and 42 months from well installation at the 4 downgradient wells followed by comparison of the measured CAH concentrations in the upgradient well at the time of initial measurement.

Table 8 Expected TCE movement at Altus AFB

Monitoring well (MW)	MW distance to biowall (m)	MW distance to upgradient well (m)	Time to MW from biowall (mo)	Time to MW from upgradient well (mo)	Sampling times (mo)
A	1.5	8.9	3	10	1, 2, 8, 16, 24, 33
B	3	10.3	7	12	1, 2, 8, 16, 24, 34
C	9	16.0	20	19	1, 2, 8, 16, 24, 35
D	30	36.0	67	42	1, 2, 8, 16, 24, 36

TCE starting at the biowall could have traveled to the first (1.5 meters) and second (3 meters) monitoring wells (MW) within a year of biowall installation. It would have taken approximately 1.7 years for this TCE to reach MW 3, 9 meters downgradient of the biowall. This means that since the TCE concentration in the biowall was 48 µg L^{-1} within the biowall in July of 2002 it would be expected that the same or less TCE would be found during the September monitoring event at MW2, 1.5 meters downgradient. This is roughly the case in that a TCE concentration of 55 µg L^{-1} was found in September at MW2 (Henry, 2008) whereas in July the reading was 290 µg L^{-1}.

Assuming the stated groundwater flow and TCE retardation factor (RF), it would have actually taken the TCE 3 months to travel from the biowall to MW1. So, the stated groundwater flow and RF may be an underestimate. Regardless, the measured TCE concentration spiked to 170 µg L^{-1} 6 months later in MW2 when it was sampled in March 2003. This information suggests that the reported biowall TCE concentrations are an artifact of high levels of TCE sorption to the biowall media. This highlights the need to consider the downgradient TCE concentrations when calculating biowall removal

capacity and or to consider the distribution coefficient for TCE when measuring TCE using a headspace volatilization method.

Following this parcel downgradient, one would expect the 55 µg L^{-1} to show up at MW 4 in March 2003 7 months after sampling in September 2002. The concentration is 130 µg L^{-1} however. This makes it difficult to interpret the data and underlies the need to clearly establish background CAH levels over the entire transect that will be used to gage biowall efficacy.

Parsons, the consulting firm involved with the project, calculated removal efficiencies for the biowall by comparing within-biowall concentrations to upgradient from the same time. The average decrease in TCE concentrations in the last sampling was 96 percent. Percent reduction in total molar concentrations of chloroethenes ranged from approximately 18 to 96 percent. The emphasis on within-biowall concentrations of chlorinated ethenes and TCE neglects the trend for total chlorinated ethenes to increase downgradient from the biowall. For example, the last two measurements show an increase in total chlorinated ethenes in MWC and MWD relative to the upgradient well. This underlies the need to report removal efficiencies based on a clearly tracked parcel of water as opposed to comparing concentrations taken from separate locations which may not have started out at the same concentration. Removal efficiencies based on downgradient well concentrations were not calculated, but would have yielded significantly lower removal efficiencies.

2.1.1 Conclusions

1.TCE levels were unquestionably decreased within the biowall as compared to the upgradient and downgradient monitoring wells. This decrease seems to have been maintained at least to 1.5 meters downgradient from the biowall.

2. *cis*-DCE was produced after TCE contaminated water passed through the biowall.

3. It is not appropriate to plot the molar concentration of TCE or total chlorinated ethenes on a graph with distance from the biowall on the x-axis and to imply or assume that the difference in concentration between the upgradient and downgradient wells is attributable to the biowall unless it has been established that the groundwater under question passed through the biowall. Otherwise, the concentration would just represent background.

4. Background contaminant levels must be ascertained and plotted along the transect that will be used to assess biowall effectiveness before monitoring for the efficacy of the biowall begins. Otherwise, assumptions about groundwater flow and TCE retardation would have to be made to confirm that the perceived treatment effects are not false positives.

2.2 Offut Air Force Base pilot scale biowall

A pilot-scale biowall was installed at Offut Air Force Base (AFB) near Omaha, Nebraska in August 2000. The groundwater contamination at the site consisted of a 3,000-ft plume with maximum TCE concentrations of 2.2 mg L^{-1} where the biowall was placed. The media used in the biowall was comprised of 50% mulch and 50% coarse sand on a volume basis. The mulch was generated at the site using shredded trees and leaves. The authors assumed an effective porosity of 0.15, making the groundwater

seepage velocity 0.23 ft day-^{1} or 7 ft mo^{-1}. Assuming a retardation factor of 2 for TCE and converting to metric, TCE would flow at 1.1 m mo^{-1}. Like the investigators of the Altus AFB biowall, GSI neglected the retardation of TCE in the groundwater and the rate of groundwater flow itself in their calculations of biowall removal efficiencies. However, these authors did establish control wells to ascertain background TCE concentrations over the study period. These wells were positioned to the south of the biowall as shown in Figure 9. In addition, the six wells used to assess the biowall were sampled right after biowall completion providing a one-time baseline sample.

Biowall performance was assessed using two upgradient, four downgradient, and two control wells sampled four times during a 19-month period. The upgradient wells were approximately 4.3 m (15 ft) from the biowall and the downgradient wells were positioned at 3 m (10 ft) and 6 m (20 ft) from the biowall . The wells were sampled starting right after installation, at 5 months, 13 months, and 19 months. Figure 9 shows the biowall and monitoring wells.

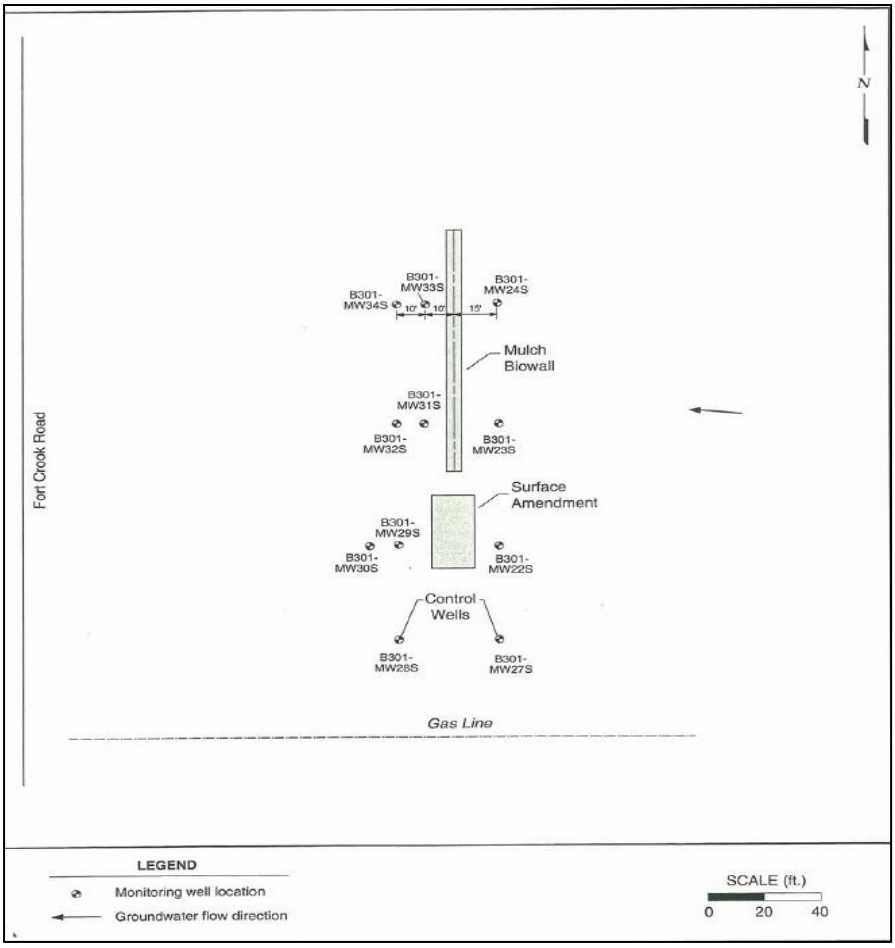

Figure 9 Offut Air Force Base pilot scale biowall illustration from GSI (2001).

A mean TCE removal rate for the 19 months of monitoring of 73% was reported for the biowall as measured by the difference in mean concentration between the two upgradient wells and the corresponding nearest wells downgradient. The calculation neglects the variation in upgradient TCE concentrations. TCE concentrations actually increased between June 1999 and August 2000 in the upgradient wells. For calculation of accurate removal efficiencies, the amount of time between sampling events should be timed to maximize the probability that TCE concentrations measured downgradient actually correspond to groundwater concentrations previously measured in upgradient positions.

For more accurate removal efficiency calculation, GSI could have compared the 1.9 mg L^{-1} found at time 0 in upgradient MW24S to the concentration found in MW33S 7.3 months later because this would have allowed the original parcel of TCE to travel the 8 m between the wells, assuming a TCE flow rate of 1.1 m mo^{-1}. Table 9 shows the expected amount of time needed for TCE to reach the monitoring wells, and the actual sampling times in months from biowall installation. Accurate calculation of removal efficiencies necessitates consideration of groundwater flow rates and the magnitude of TCE retardation.

Table 9 Expected TCE movement at Offut AFB

Monitoring well (MW)	MW distance to biowall (m)	MW distance to upgradient well (m)	Time to reach MW from upgradient well (mo)	Sampling times (mo)
A	3	8	7.3	0, 5, 13, 19
B	6	11	10	0, 5, 13, 19

Five months after installation, DCE was clearly being produced based on the two order of magnitude increase in the mean ratio of DCE to TCE that occurred in the downgradient wells. After this time, the DCE:TCE ratio declined as did the amount of DCE produced. Despite the decrease in DCE production over time, GSI found that total mean chlorinated constituents decreased by 60% between the upgradient and nearest downgradient monitoring wells whereas the control plot had a mean percent increase of 12%.

Groundwater Services, Inc. calculated the amount of TCE and total chlorinated solvent removal that could be attributed to daughter and end product formation. The calculation showed that only 25% of degraded TCE could be linked to *cis*-DCE, VC, ethene, and ethane. In addition, complete anaerobic dechlorination of TCE to ethene and

ethane accounted for only 10% of total dechlorination. This low molar balance could be caused by losses of the most volatile metabolites VC, ethene, and ethane to the unsaturated zone. Furthermore, aerobic microenvironments within the aquifer may have permitted aerobic biodegradation of daughter products resulting in the formation of acetylene. Finally, sorption may be responsible for immobilizing TCE and its daughter products in the mulch biowall or the aquifer solids.

Sorption is not a permanent solution to groundwater contamination with TCE. Any given reactive matrix has a limited capacity to absorb the contaminant and its byproducts indicated by its point of saturation. Moreover, once the concentration of TCE decreases below a critical threshold, desorption will occur and the contaminant will re-enter groundwater (Zytner 1992). Despite these shortcomings of sorption as a treatment method, sorption may still enhance microbially mediated degration of TCE because most degradation occurs on surfaces rather than in solution.

2.2.1.1 Conclusions

1. Like the Altus AFB pilot biowall, the Offut AFB biowall erroneously calculates removal efficiencies by failing to consider groundwater flow and TCE retardation; however, control wells were used to establish background TCE concentrations across the biowall site.

2. The authors calculated a molar balance for chlorinated ethenes passing through the biowall which shows that only 25% of degraded TCE could be linked to its anaerobic daughter products. Suggested explanations include loss of volatile degradation products to the unsaturated zone and or oxidation of daughter products in aerobic microenvironments within the groundwater.

3. Ignoring the errors in calculation of removal efficiency for TCE by the biowall, the average removal efficiency between the upgradient and nearest downgradient wells was about 70%. The biowall successfully stimulated reductive dechlorination as evidenced by the 2 order of magnitude increase in the DCE to TCE ratio between the upgradient and 10 ft downgradient monitoring wells. Complete dechlorination of TCE to ethene and ethane was observed; however, complete dechlorination did not occur until sulfate-reducing and methanogenic conditions were reached.

2.2.2 Seneca Army Depot Biowall, New York

A permeable mulch biowall pilot test was implemented at the Ash Landfill at Seneca Army Depot Romulus, New York to test the efficacy of this approach compared to a ZVI PRB already installed at the site. The plume of chlorinated solvents at the site extended approximately 1,100 feet from the landfill and was comprised mostly of TCE and *cis*-DCE. Concentrations of total chlorinated ethenes in January 2006 reached up to 2.088 mg L^{-1}. The material used in the biowall consisted of 200 cubic yards of shredded whole deciduous and evergreen trees and 150 cubic yards of sand mixed together. The direction of groundwater flow is east to west. As an experiment, two biowalls were installed in tandem, the eastern one separated from the western wall by 10 feet. The mulch-sand mix for the west Biowall was coated with 880 gallons of soybean oil before putting it into the trench. Assuming an effective porosity of 20 percent just as the authors did produces an average linear water velocity of 0.125 ft day^{-1} or 1.5 ft mo^{-1}. This reduces to 0.23 m mo^{-1} if one assumes a TCE retardation factor of 2 and converts to metric.

The two parallel biowalls were installed between July 18th and 22nd and groundwater monitoring commenced with the installation of 11 monitoring wells in August 2005. Post-installation sampling of an existing and the new monitoring wells continued in September 2005, October 2005, December 2005, and January 2006. Although the pilot biowall was only tested for 5 months, the results of the pilot investigation apparently warranted full scale application of the mulch biowall at the site. The monitoring wells were positioned 3.7 m (13 ft) upgradient from the wall, within the first wall, 2 m (7.5 ft) downgradient from the first wall, within the second wall, 2 m (7.5 ft) from the second wall, and 6.4 m (22.5 ft) from the second. The biowalls and monitoring wells are illustrated in Figure 10.

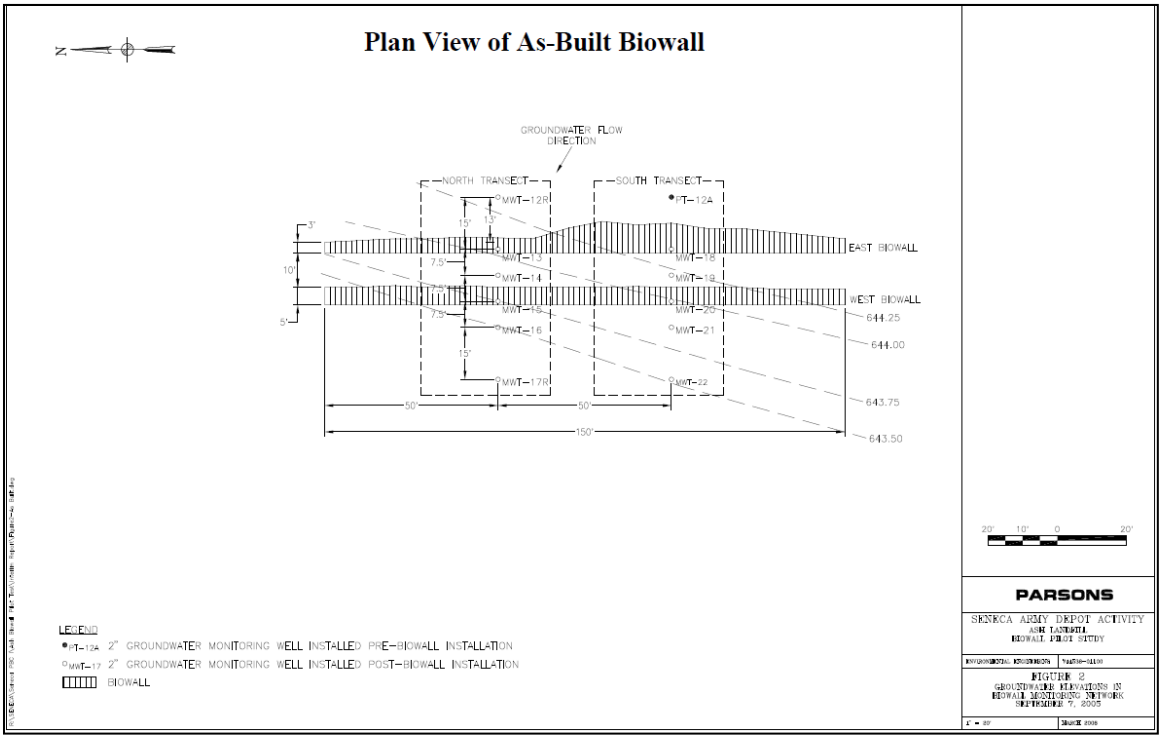

Figure 10 Biowalls and monitoring wells at Seneca Army Deport (Henry 2008).

Considering the rate of groundwater flow and a minimum TCE retardation factor of 2, the TCE concentrations measured in all downgradient wells do not reflect the

treatment effect of the biowall because it should have taken 10 months for TCE within the biowall to reach even the nearest downgradient monitoring well at 2.3 m (7.5 ft). This idea is represented in Table 10, which shows the expected movement of TCE at Seneca Army Depot. Sampling took place 1, 2, 3, and 5 months after biowall installation.

After 5 months, the TCE within the biowall would have only moved 1.1 m (3.75 ft) within the aquifer. Regardless, background concentrations along the transect were not established prior to monitoring so it is unknown the extent to which the observed TCE decreases along the two transects are the consequence of the biowalls. Aside from potential errors in data interpretation, the data show that within the biowalls TCE concentrations were greatly depressed to the point of non-detect while downgradient monitoring wells had higher concentrations ranging from 2.9 $\mu g\ L^{-1}$ to 25 $\mu g\ L^{-1}$. At 13 weeks, total chlorinated ethenes in both downdgradient transects shot up to around or above upgradient levels.

At 27 weeks, the CAH profile had become more diverse as c-DCE degraded to VC and VC to ethene. One explanation for this behavior is that the biowalls reached saturation and then began to desorb the TCE causing the observed increase in chlorinated ethene concentrations downgradient of the biowall. Henry (2008) reported that the percent reduction in total molar concentrations of chloroethenes along the study transects ranged from 86 to 99 percent over time, but this statistic only considers within-biowall concentrations compared to upgradient from the same time.

In both transects, total molar concentrations of chloroethens appear clearly depleted within the biowalls and a decrease is observed in the North Transect downgradient as well. However, along the South Transect there was a general increase in

total chlorinated ethene concentrations. The increase in molar concentration downgradient from the South Transect biowalls is explained as desorption of TCE from native soils, mixing with untreated groundwater, and or indication that biodegradtion may be limited to the immediate biowalls reactive zone. Again, it may be misleading to report biowalls effectiveness in terms of within-biowall concentrations. In addition to the role of sorption in lowering within-biowall concentrations, is volatilization through the biowall media, which may be more permeable than the native soil. This hypothesis can be tested in the future with mass balances and possibly by measuring soil gas over the biowall as compared to the upgradient soil.

Table 10 Expected TCE movement at Seneca Army Depot

Monitoring well (MW)	MW to from East biowall (m)	MW distance to upgradient well (m)	Time to reach MW from biowalls (mo)	Time to reach MW from upgradient well (mo)	Sampling times (mo)
A	2.3	6.85	10	31	1, 2, 4, 5
	Distance from West biowall (m)				
B	2.1	12	10	55	1, 2, 4, 5
C	6.4	16	30	75	1, 2, 4, 5

2.2.2.1 Conclusions

1. As in the other case studies, the authors fail to consider the effects of groundwater flow rate and TCE retardation on perceived TCE removal efficiencies. Additionally, neither control wells nor background contaminant concentrations were established along the transects in question making it difficult to accurately decipher biowall treatment effects.

2. A clear increase in TCE anaerobic degradation byproducts was observed over time indicating that the biowall effectively spurred anaerobic dechlorination, but that it took time (27 weeks or ~6 months) for the microbial population and or the redox condition in the aquifer to become acclimated. It is unclear how the rate of complete TCE

degradation is dependent on microbial acclimation, oxidation reduction potential, or whether it is a combination of a sufficiently low redox state combined with the microbial population adapted to this state.

2.3 Overall Conclusions

For the two sites with monitoring wells within the biowalls, the concentration of total chlorinated ethenes was reduced a minimum of 85% in the biowalls when compared to upgradient monitoring wells. TCE concentrations 3 m downgradient from the biowalls were reduced compared to upgradient concentrations measured concurrently, but were generally higher than within-biowall concentrations. Furthermore, in some cases downgradient total chlorinated ethene concentrations increased possibly due to desorption of TCE sorbed to native soil or because of errors in data interpretation.

For all the biowalls, concentrations of TCE degradation byproducts increased dowgradient from the biowalls, suggesting that the biowalls spurred some level of biological reductive dechlorination. However, due to the absence of baseline data for two of the sites and the failure to account for fluctuating upgradient TCE concentrations, it is difficult to clearly interpret these data. The chlorinated ethene mass balances and control wells established at Offut AFB were useful tools for understanding biowall efficacy and should be employed in the future.

At all three sites, there remains a question as to the exact conditions that allow complete degradation of TCE although it appears that redox conditions sufficiently low for sulfate reduction and methanogenesis are needed for TCE to be fully reduced to ethene. Future research efforts should focus on understanding whether a sufficiently low redox state and adapted microbial community (e.g. sulfate and CO2 reducing bacteria)

can totally and efficiently degrade TCE or whether very specific microbial populations are needed. If it becomes clear that sufficiently low redox state is the deciding factor, then decreasing ORP as quickly as possible will become the primary objective in biowall –based remedial actions.

2.4 Recommendations

1. Sample along the transect that will be studied before installing the biowall as many times as possible to establish baseline trends.
2. Clearly establish seepage velocity and TCE flow rates along the study transect before biowall installation
3. Devise monitoring regimens and calculate biowall removal efficiencies based on the expected flow rate of TCE in the aquifer.
4. As done by GSI for the Offut, AFB biowall, CAH mass balances may be used to better understand the capacity of biowalls to fully dechlorinate CAHs and DCE:TCE ratios may be used to gage biowall effectiveness.

Chapter 3:Methods

3.1 Site Data Analysis

For the site data analysis, I have compiled and independently evaluated site data collected by BMT Entech between 1997. The site data is presented along with the original interpretation of the data followed by my interpretation plus a brief quality assessment. These data include groundwater, surface, soil and sediment, soil gas, and modeling output. I also review data quality and interpretation. The purpose of the site analysis is to understand the reasoning behind the selected remedial action and to decide whether it meets the USEPA goal of protecting human health and the environment.

Using GIS to visualize the site data, I provide spatial and temporal representations of groundwater contamination at the site, which permits heightened understanding of contaminant behavior. The surface water, soil, and sediment, and soil gas data are presented to provide the clearest possible picture of the contaminated site. Moreover, these data are used to further understand the site site-specific spatial and temporal aspects of contaminant transport. I consider the potential for natural attenuation shown by the data mainly in the form of reactive soil and dissolved iron. Finally, I present the BIOCHLOR model as run by BMT Entech and using altered input parameters. Throughout the analysis I relate the original and revised data interpretation to the question of whether the chosen remedial action and preceding decision making process protect human health and the environment.

3.2 Batch Study Experimental Summary

The batch study was conducted to provide guidance for the selection of biowall materials and as a tool to assess whether the chosen remedial action could provide significantly better treatment than the site soil. To achieve these ends, 10 individual treatments were used. Seven of which related to the first admixture (MX1) and three of which to the second admixture (MX2). A full list of treatments is presented in Table 11. The effectiveness of each treatment to fully degrade TCE was determined by calculating rates of degradation and total loss of chlorinated ethenes. Both metrics were derived based on measurement of chlorinated ethenes in the headspace of the microcosms using a GC/MS analyzer by USEPA-accredited Maryland Spectral Services. Total system TCE and daughter products were determined using calculated values for dimensionless Henry's constant and solid partitioning coefficient at 10°C for each compound.

Table 11 Experimental design matrix

Sample Label	Media	Replicates	Glycerol Dose (mL L^{-1} solids)	ZVI Dose (ml L^{-1} solids)
Sand BLK	Autoclave Sand Blank	1	0	0
Sand SPK R1, R2, R3	Autoclaved Sand Spike	3	0	0
Soil SPK R1, R2, R3	Native Soil Spike	3	0	0
M1/C1: G0 + Fe0 R1, R2, R3	1:1 Mix	3	0	0
M1/C1: G10 + Fe0 R1, R2, R3	1:1 Mix - Gly L1	3	10	0
M1/C1: G30 + Fe0 R1, R2, R3	1:1 Mix - Gly L3	3	30	0
M1/C1: G0 + Fe10 R1, R2, R3	1:1 Mix - Fe L1	3	0	10
M1/C1: G0 + Fe100 R1, R2, R3	1:1 Mix - Fe L2	3	0	100
M1/C1: G10 + Fe10 R1, R2, R3	1:1 Mix - Gly FeL1	3	10	10
M1/C1: G30 + Fe100 R1, R2, R3	1:1 Mix - Gly FeL3	3	30	100
M5/C1: G0 + Fe0 R1, R2, R3	5:1 Mix	3	0	0
M5/C1: G10 + Fe0 R1, R2, R3	5:1 Mix -Gly L1	3	10	0
M5/C1: G0 + Fe10 R1, R2, R3	5:1 Mix - Fe L1	3	0	10

3.3 Hydraulic Conductivity

Hydraulic conductivity of the biowall media was measured using the falling head permeability test for sand (Das 2002). The test was conducted on MX1 and MX2 which were comprised of 30% compost, 30% mulch, and 40% sand and 10% compost, 50% mulch, and 40% sand respectively (Table 11). The test was performed using two different columns for each treatment with a minimum of four replications performed on each column.

3.4 Biowall Nutrient Analysis and Material Description

The compost blend used was comprised of 10% food residual compost and 90% leaf compost. Both materials were generated at the Beltsville Agricultural Research Center (BARC) and stored prior to use at the old BARC airport site. The composts were sent to PENN State Agricultural Analytical Services Laboratory for physio-chemical analysis. The tests included percent solids, organic matter, pH, soluble salts, total nitrogen, total carbon, carbon:nitrogen ratio, ammonium nitrogen, phosphorus, potassium, aluminum, calcium, magnesium, sodium, copper, iron, sulfur, and zinc.

The mulch used was obtained from the BARC compost research facility where it had been stored since the summer of 2010. The mulch was 1 inch in diameter or less and created from tulip poplar. The organic matter content of the wood chips was determined using loss on ignition. Dry woodchips were placed in a muffle furnace at 550 °C for 4 hours. The percent organic carbon was calculated as half of the weight lost from ignition. This assumes that about half the weight of the lost organic matter was comprised of carbon. We used concrete sand as the coarse aggregate material in the biowall mixes. The material was obtained from a storage area at BARC.

The glycerol used in the study was obtained from Emergent Industrial Solutions, LP a glycerin retailer based out of Texas. Most of their glycerin is produced as a co-product of biodiesel production. According to their product specifications, the glycerin was at least 78% glycerin by weight and a maximum of 13% water. A glycerol content of 80% was used in the initial carbon balance and all other calculations. The product may have contained up to 0.03% methanol and had a pH between 5 and 8. As a source of zero-valent iron (ZVI) we used iron aggregate ETI $CC^{-1}004$ (-8+50) obtained from

Connely-GPM, Inc. The material is derived from ground up cast iron and contains iron particles of varying sizes and valence though mainly zero valent being derived from metal.

The site soil used in the batch study came from soil borings made by BMT Entech in March 2011. Two boring locations, 6 and 16, were chosen because they are not located in TCE hotspots. The portions of the borings within the saturated zone were used which included 2 to 12 ft for boring 6 and 4 to 12 ft for boring 16. The borings were combined in equal volumes and mixed thoroughly for the background soil mixture. However, after restarting the experiment because of errors in spiking and having one soil background jar fail, it was necessary to add more of soil bore 6 because 16 was completely used up. Thus, the third replicate of the soil background had approximately 75% soil bore 6 and 25% soil bore 16 by volume.

3.5 Experimental Set Up

Each reactor was comprised of a 1 liter jar, 0.5 L of solids, 0.3 L site groundwater, and 30 µg of TCE. The remaining headspace was approximately 0.4 L due to the porosity of the biowall mixtures. All the jars were sterilized in an autoclave prior to use. The solids including the mulch, compost, and sand were first weighed and added to the jars followed by amendments of ZVI and or glycerol. The baseline mixtures MX1 and MX2 were created in 5 gallon sized batches prior to jar set-up. For each baseline mix, the components were mixed in 2 L increments and each 2 L addition was created by adding a third of the volume at a time and tamping the beaker 10 times. Volume reduction in the admixtures was calculated by measuring the volume of each freshly made admixture and comparing re-measured volume to the expected volume.

The glycerol was added to the jars just prior to the water and initiation of the experiment to minimize its degradation prior to the start. Then 0.25 L of background groundwater, which was confirmed to have no detectable contaminants, was added directly to the jars. Next, the jars were capped and removed of air to the point of vacuum. The vacuum facilitated spiking with the TCE. The TCE was added as a 50 mL spike at a concentration of 600 µg L^{-1} directly into the jar with 0.25 L of groundwater via a syringe port in the jar lid. This brought the starting concentration to 100 µg L^{-1} chosen because this is the upper limit of the GC-MS calibration range. Subsequently, the jars were re-pressurized to just above ambient pressure. Figure 11 displays various parts of the experimental set-up including from top left going clockwise, jar pressurization, storage at 10 ºC in the wine coolers, attachment for GC-MS sampling, and a profile of a sand spike and MX1 with ZVI amendment.

The amendment dosages were apportioned on a volumetric basis in terms of milliliters of amendment per liter of base mix. Amendments were added volumetrically rather than on a mass basis because this simulates the field mixing procedure which would be performed volumetrically using the bucket of a tractor or back-hoe. Three levels for each amendment were tested for MX1. For glycerol, these included 0 ml L^{-1}, 10 ml L^{-1}, and 30 ml L^{-1}. For ZVI, these included 0 ml L^{-1}, 10 ml L^{-1}, and 100 ml L^{-1}. To test interaction effects between glycerol and ZVI, we used two combined treatments. One with the low glycerol and ZVI dose, and one with the high. Due to monetary limitations, and because it was hypothesized that MX1 would outperform MX2 only the low dosage of glycerol and ZVI were tested for MX2.

The glycerol doses were based on previous biowalls with emulsified vegetable oil amendment. The range of previously used liquid carbon amendments used is 2 to 5 gl yd^{-3} which converts to approximately 10 to25 ml of glycerol per L of solids. Thus the chosen glycerol doses reflect the low and high parts of this range. ZVI has not been previously used in biowalls so there was not a clear historical precedent to base the dose on. ZVI has been used in permeable reactive barriers however, composing 50% of the volume with some coarse additive such as sand occupying the remaining space (Henry 2008). Considering that the final amount of material needed for the BDRLF is about 2000 yd^3or 1520 m^3, adding ZVI at a rate of 1% (low dose) would still require total ZVI-volume of 20 yd^3 or two dump truck loads. At $4 per pound or $52,500 per cubic yard, 20 yd^3 of ZVI would cost over 1 million dollars. Regardless, this rate was taken as the minimum relevant amount of ZVI and chosen as the low dose while 100 ml L^{-1} was chosen as the high ZVI dose. The high dose is not practical for large biowalls due to the cost of ZVI, but was worth considering for smaller biowalls or different designs.

Figure 11 Examples of the experimental set up.

In addition to the tested biowall media and amendments, we tested the site soil and pure concrete sand. The site soil was meant to show levels of in-situ degradation and provide a reference for assessment of the performance of the biowall treatments. The

sand spike was meant as a negative control. As shown in Table 11, there were a total of 10 treatments, seven for MX1 and three for MX2. With three replicates for each treatment plus three replicates for the background site soil and sand spikes there were a total of 36 experimental units (jars).

Sampling was staggered over the course of three days due to time limitations. Each of the tree replicates for the 10 treatments were measured on a different day. Nine samples were taken from each jar over the course of this period. The jars were stored in unmodified wine coolers set to 10°C for 144 days to simulate groundwater conditions. This represents a marked difference from past batch and column studies of biowall performance because all known maintained reactors at 20°C to 25°C. The coolers blocked most light. Temperature was monitored with watchdog sensors and recorded every two hours.

3.6 Mass Balance

Mass balances were used as both a quality assurance check and as a means of anticipating partitioning between solid, liquid, and gas phases. A mass balance for the sand spike was used as a quality assurance check because it was assumed that all of the TCE added to the sand microcosms partitioned into the aqueous or gaseous phase. After one week, we assumed that all the TCE in the sand spikes partitioned into the headspace and aqueous phase as governed by Henry's Law at 10 °C. Since we added 30 µg to each jar initially, the mass balance should indicate a value close to 30 µg in the gas and liquid phases. After evaluating this assumption, the sand spike could be used as a basis for calculation of solid partitioning in the other microcosms. The mass balance for the sand spike was $M_T = C_L V_L + C_G V_G$.

The first step in the calculation of the quality check mass balance was to convert the headspace concentration from ppbv to µg L^{-1} using the ideal gas law at 10 °C. To obtain the aqueous phase concentration, Henry's law was employed. The dimensionless Henry's constant was derived using the equation developed by Heron et al. (1998) at 10 °C. The constant calculated was 0.16. Dividing the headspace concentration by 0.16 yielded the aqueous concentration in µg L^{-1}. From here, I calculated the mass of TCE in the sand spikes by multiplying the volume of headspace and liquid by their respective TCE concentrations and summing as shown in the mass balance above.

Another set of mass balances was created to predict partitioning of TCE in the other microcosms. The mass balance was formulated using the equation $M_T = C_L V_L + C_G V_G + C_S M_S$. The starting liquid, solid, and gaseous volume was 0.3, 0.5, and 0.4 L. Dimensionless Henry's constant ($H^{'}$) was the same as above. To determine partitioning, the mass balance was rewritten as $M_T = C_L{*}V_L + [C_L{*}H'] \text{ Vair} + K_d{*}C_L{*}M_S$ and solved for C_L. Once known, C_G was calculated using Henry's Law and the mass sorbed to solids was calculated assuming a linear adsorption isotherm.

The distribution coefficient (K_d) used to estimate solid partitioning was calculated using an organic carbon partitioning coefficient derived by Shen and Wilson (2007) using biowall material with similar make-up to the ones used here. The calculation of K_d was made assuming the relationship $K_d = K_{oc}{*}f_{oc}$. The fraction organic carbon (f_{oc}) was obtained for MX1 and MX2 by dividing the carbon mass by the total mass for three replicates and averaged. The carbon mass was derived by measuring the organic matter mass lost on ignition at 550 °C for three replicates of each mix and dividing by two assuming approximately 50% of the organic matter mass lost was carbon (Brady and

Weil 2008). Due to variations in the average f_{oc} for MX1 and MX2, two different K_d values were used.

3.7 Groundwater Analysis

The groundwater used was collected from MW4. We removed the water with a peristaltic pump run by a gas powered generator. MW 4 represents background groundwater conditions at the site because it is not impacted by flow from the landfill. We measured depth to groundwater, dissolved oxygen (DO), temperature, pH, oxidation reduction potential (ORP), conductance, and turbidity at the time of measurement using an Horiba U-10 Water Quality Checker.

3.8 Batch Study Data Analysis

I assessed the ability of each of the10 batch treatments to degrade TCE by calculating total TCE mass removed from the jars after 144 days. The percent mass of TCE removed was identical to the percent reduction in headspace concentration, but this measure does not consider the 25 ml headspace removal at each of the 9 measurements. So, TCE mass degraded had to be calculated by subtracting the mass removed during sampling. The TCE removed during sampling was calculated by multiplying 25 ml by the concentration of TCE in the headspace at the time of measurement.

The concentration had to first be converted from units of ppbv to $\mu g\ L^{-1}$ using the ideal gas law at 10°C. The calculation of percent degradation was made using the TCE mass after five days as the M_0 and the mass after 144 days as M_{final}. The treatments were compared using the average, standard deviation, and variance of the three replicates. The

average degradation efficiencies were compared using bar graphs. Qualitative data analyses included interpretation of outliers and other anomalous results.

Chapter 4: Results and Discussion

4.1 Site Data Analysis

Table 12 displays the tests and methods used to analyze the soil, sediment and groundwater samples taken at BDRLF. TCL stands for Target Compounds and Analytes, a set of compounds that the USEPA has designated as priority pollutants. For baseline monitoring well sampling (1997), all the tests for groundwater were applied. The SSP included monitoring well sampling, geoprobe well sampling, and surface water and sediment sampling. Surface soil, subsurface soil, surface water and sediment samples were analyzed according to Table 12, but SVOCs, pesticides, and PCBs were excluded from the groundwater tests because they were not previously detected in the monitoring wells during the Baseline Groundwater Study. The RI included all the tests represented in Table 12.

Table 12 Tests and methods for soil, sediment, and groundwater analysis at BDRLF

Matrix	Test	Method
Surface Soil	TCL VOCs	SW8260B
	TCL SVOCs	SW8270C
	TCL OC Pesticides	SW8081A
	TCL PCBs	SW8082
	Chlorinated Herbicides	SW8151A
	TAL Metals	SW601B/7471A
	TOC	Loyd Kahn
	pH	SW 9045C
Subsurface Soil Groundwater Surface Water Sediment	TCL VOCs	SW8260B
	TCL SVOCs	SW8270C
	TCL OC Pesticides	SW8081A
	TCL PCBs	SW8082
	Chlorinated Herbicides	SW8151A
	TAL Metals	SW601B/7471A

4.1.1 Soil Gas Survey

As part of the RI, BMT Entech conducted a soil gas survey in November 2002 to identify likely locations of VOC contamination within the shallow aquifer. This data was used to select optimum locations for subsequent soil borings and the installation of additional monitoring wells, and to provide a preliminary indication of the magnitude and extent of VOC contamination at the site. Samples were collected from 3-8 feet below ground surface based on the sampling grid shown in Appendix A, Figure A-1. Initially, 32 soil gas locations were sampled. Subsequently, an additional 20 locations were sampled based on the results of the first round of samples. In the end, 62 samples including duplicates were taken. Sample analysis was performed at a nearby base support laboratory equipped with a gas chromatograph and other appropriate analytical equipment.

Soil gas results for TCE and PCE, the most commonly detected compounds, are shown in Figure 14 and Figure 15 in maps made by BMT Entech which assume decreasing concentric circles of concentration around contaminant hotspots. For TCE, there were two hotspots; one centered approximately 256 ft south-southwest at B4, and the other centered approximately 164 ft southeast at G2. As shown in Figure 12 and Figure 14, there was one other location where TCE was detected at trace levels between the two hotspots at E4. In the RI, BMT Entech generally refers to the VOC hotspots lumping TCE, PCE and a number of VOCs together. They state that these hotspots were 140 feet south-southwest and the other 120 feet southeast. These numbers differ from the ones presented here. The shortest distance between the TCE hotspot at B4 in Figure 12

and the landfill boundary is 78 m or 256 ft rather than 140 feet. The distance between the second TCE hotspot at G2 was found to be 50 m or 164 ft rather than 120 ft.

It is unclear how BMT Entech arrived at their distance measures, but here I have presented the distance between the un-vegetated boundary of the landfill and the center of each hotspot, measuring the distance in ArcMAP 10.0. PCE hotspots were found in three regions as shown in Figure 15 and Figure 12. The southeast hotspot preceded the TCE hotspot by about 115 ft occurring at F2 while the southwest hotspot was well aligned with the TCE at B4. The third and largest hotspot where PCE was found was centered approximately 298 feet south of the toe of the landfill at point EF45. BMT Entech does not appear to have used the correct concentration in their map so Figure 15 is incorrect. Figure 12 has the correct value.

PCE was more prevalent in soil gas in terms of concentration and frequency of detection. Groundwater sampling has showed little PCE, an observation that BMT Entech attributed to 6 times lower solubility of PCE and its higher Henry's Constant. Some of the highest concentrations of VOCs in soil gas were detected at grid locations A-4 and B-4. However, groundwater sampling one year later and soil sampling 5 months later showed no VOCs in this region. MW3 was placed in the center of this hotspot, but has never yielded VOC contaminated water. This could be due to volatilization through the soil surface, losses due to volatilization during flooding, migration, or some other form of natural attenuation such as transpiration by trees or biogeochemical degradation. Regardless, the disappearance of these contaminants indicates natural attenuation of one form or another, rapid migration of the contaminants off the site, or failure to detect them due to choice of sampling location.

The interpretation of the soil gas survey provided by BMT Entech was limited to the already mentioned information. By remapping the soil gas data in ArcGIS I have made a number of observations and interpretations. Contrary to the low likelihood of natural attenuation predicted by BMT Entech based on the BIOCHLOR model and groundwater sampling (BMT Entech 2008b), the soil gas survey showed significant evidence of chlorinated solvent degradation most notably at sampling points A4, B4, and G2. At these three sites shown in Figure 12 and Figure 13 the possible parent compounds PCE and PCA were found along with most or all of the degradation byproducts expected under biotic or abiotic reducing conditions. For example, at G2 there was 71.44 µg L^{-1} PCE, 75.5 µg L^{-1} TCE, 59.3 µg L^{-1} *cis*-DCE, 36.68 µg L^{-1} 1,1-DCE, and 19.01 µg L^{-1} *trans*-1,2-DCE for the chlorinated ethenes and 41.98 µg L^{-1} 1,1,1-TCA, 46.32 µg L^{-1} 1,1-DCA, 57.02 µg L^{-1} 1,1,2,2-PCA for the chlorinated ethanes plus 99.05 µg L^{-1} of 1,2-DCP, which may or may not be related to the other chlorinated solvents. Vinyl chloride did not show up in any of the soil gas samples.

The co-occurrence of these CAHs indicates that the site is capable of natural degradation without intervention, an observation supported by the experimental work discussed in the next section. Both PCE and 1,1,2,2-PCA are known to degrade under similar conditions and the role of reactive iron has been established in a number of studies(Jung and Batchelor 2008, Butler and Hayes 2000). In addition 1,1,2,2 PCA can degrade directly to *cis*-DCE and *trans*-DCE by reductive β–elimination or indirectly from the intermediate TCE via hydrogenolysis (Jung and Batchelor 2008).

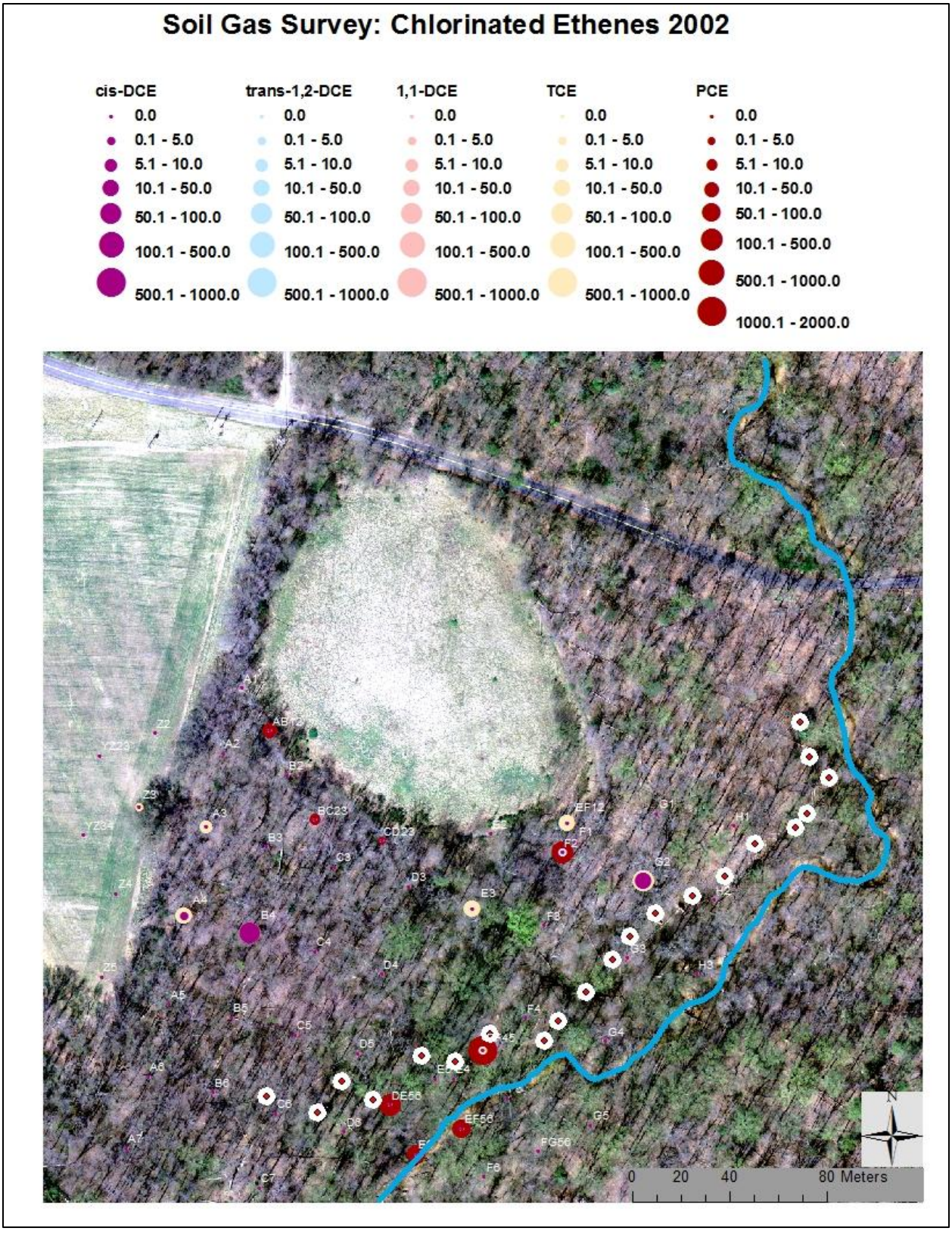

Figure 12 Chlorinated ethenes detected during 2002 soil gas survey.

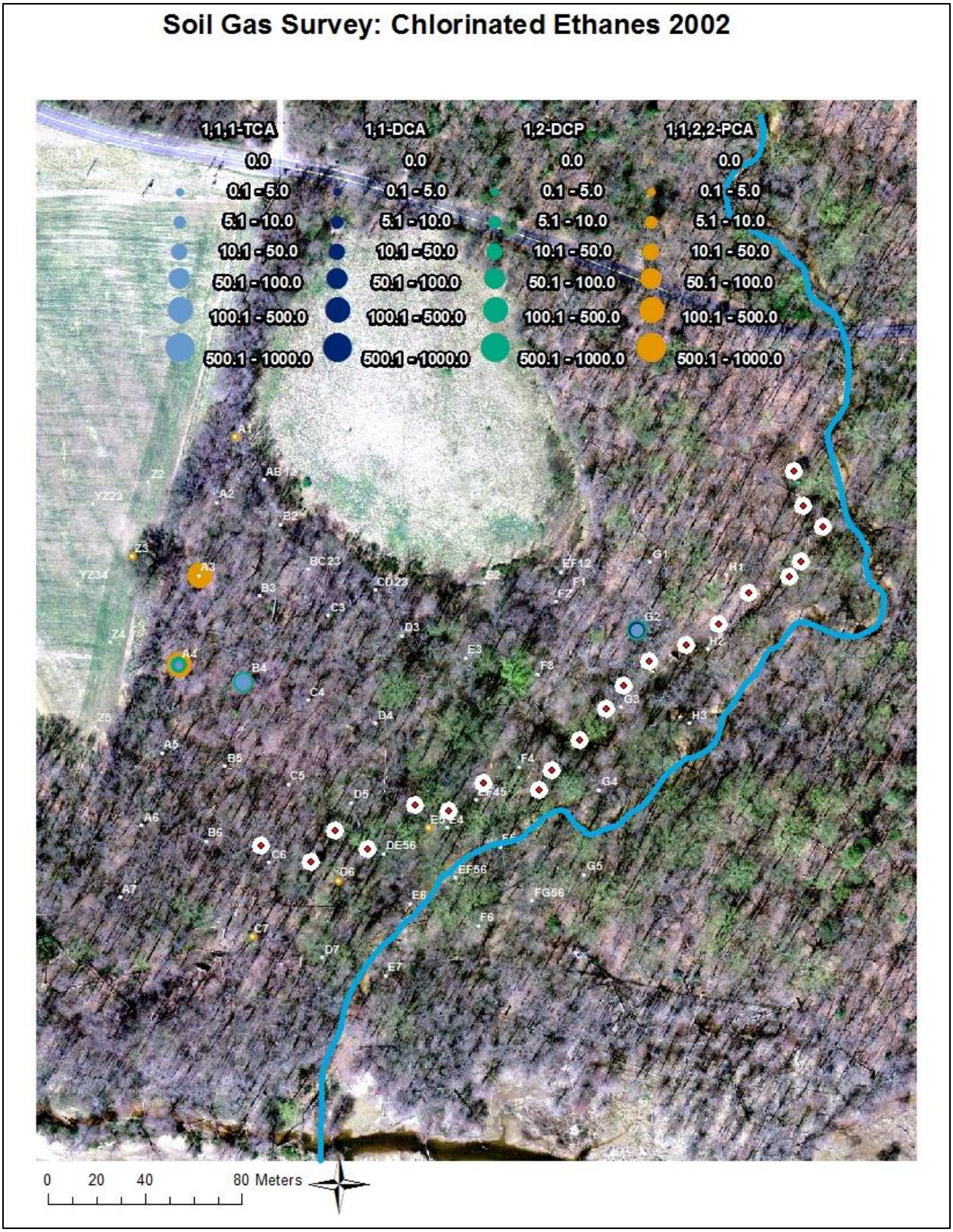

Figure 13 Chlorinated ethanes detected in the 2002 soil gas survey.

The overlapping colored points in Figure 12 and Figure 13 provide a visual of the probable degradation occurring at the site. Although these degradation byproducts have been found in the groundwater at the site since the start of monitoring the concentrations are much lower. This is probably due to the higher volatility of the degradation byproducts relative to the parent compound TCE combined with extremely shallow groundwater and periodic flooding. As mentioned in the RI (2008b), PCE has been detected to a lesser extent than TCE in the groundwater probably because it is less soluble and has higher volatility than TCE despite its greater size.

Not mentioned in either the Tidewater Inc. report or the RI is the 1054.68 μg L^{-1} PCE found at point EF45 (Figure 12). In 2002, this PCE was approximately100 m from the landfill in the direction of groundwater flow. If the PCE came from the landfill and traveled via groundwater in the saturated zone it would have taken about 75 years at the fastest documented seepage velocity of 1.34 m yr^{-1}. This means it would have been deposited in 1927, which is not possible since the landfill was not in commission. Another more likely possibility is that it was deposited closer to the site where it was detected. This may be true for points EF58, DE58, and E6 all of which are even further from the landfill than EF45. None of these points would benefit from the biowall based on its placement shown in Figure 12 by the white-red points and it is unlikely that this contamination is still at the site based on the proximity to the creek and the volatility of PCE.

Another source of evidence that the site contamination did not originate in the landfill is detection of TCE, PCE, and PCA at Z3 plus numerous degradates in A3 and B4. Point Z3 is not in the flow path of the landfill and A3 and B4 may not be based on

the flow path shown in Figure 2. They may originate from somewhere in the agricultural field or somewhere at its fringe where it is possible old farming equipment was buried. 1,1,2,2-PCA was once commonly used as a refrigerant. It is possible that at least at points Z3, A3, and A4 it originates from buried refrigerators or freezers. Considering that the concentration of 1,1,2,2-PCA is at least six times higher than all the other detected VOCs in A4 and about 30 times higher in the nearby point A3, it seems probable that at least in this vicinity the origin of the contamination is 1,1,2,2-PCA from a refrigerator or some other cooling unit buried in the ground that is degrading to known metabolites. The presence of PCE at these locations complicates this view as it is not a known degradate of 1,1,2,2-PCA. One possible explanation is that lower levels of PCE were disposed of along with the refrigerator or cooling unit.

The soil gas survey showed TCE and the other PCE daughter products did not occur independently of PCE in most cases. Only two instances of TCE detection independent of PCE were made at points E3 and EF12. This is another indication that the subsurface at the site is capable of reducing chlorinated solvents. Of course, it is possible that the co-occurrence of these compounds is merely coincidence and that they actually originate from different sources; however, due to the relative isolation of the points of soil gas contamination it is more probable that these contaminants are related in origin.

In addition to the co-occurrence of PCE and related daughter products, is the co-occurrence of chlorinated ethanes and ethenes. For example, the largest concentrations of chlorinated ethanes occur at the same locations as significant chlorinated ethene detection points as shown in Figure 12 and Figure 13 at points A3, A4, B4, and G2. A3, A4, and B4 are not in the immediate flow path of the landfill, suggesting that the contaminants at

these points originate from buried debris close to these points. The 1,2-Dichloropropane (DCP) found to co-occur at A4, B4, and G2 may come from fumigants used for agricultural purposes buried along with the source of the chlorinated ethenes and ethanes or may stem from the same source as 1,2-DCP was also used as a solvent, paint stripper, and varnish (ATSDR 2011a).

4.1.1.1 Conclusion

The initial interpretation of the soil gas survey by BMT Entech was limited and flawed as it only minimally discussed the PCE and TCE found at BDRLF. An example of the erroneous data interpretation is seen by the distance from the landfill the two PCE and TCE hotspots were stated to be from the landfill. They were said to be 140 feet south-southwest and 120 feet southeast when in actuality the distances appear to be 256 ft and 164 ft for TCE and 256 ft and 75 ft for PCE plus another peak 298 ft south of the landfill. The co-occurence of chlorinated ethanes and ethenes and multiple degradates of PCE and or 1,1,2,2-PCA was not explored at all. Moreover, significant occurrences of PCE along the creek about 115 meters south of the landfill were not mentioned at all. The highest PCE concentration of 1054.68 $\mu g\ L^{-1}$ detected at the site occurred in this vicinity at point EF45.

Contrary to previously conceived notions of the site, the re-interpretation suggests that there is strong evidence that some of the contamination detected at the site did not flow from the landfill. This is due to the location and or distance from the landfill of the detected contaminants in relationship to the landfill boundaries and the groundwater flow direction determined by BMT Entech. This statement is also based on the conservative assumption of the faster of two groundwater flow rates determined for the site. Finally,

the soil gas survey provides evidence for significant natural attenuation of chlorinated ethenes and ethanes at the site in the form of the co-occurrence of PCE, 1,1,2,2-PCA, and most of their abiotic and biotic anaerobic dechlorination byproducts. Not every point with significant PCE or 1,1,2,2-PCA showed above trace levels of degradates, but three of the locations showed the occurrence of significant degradation byproducts indicating that conditions are amenable at least in some regions of the site to natural attenuation.

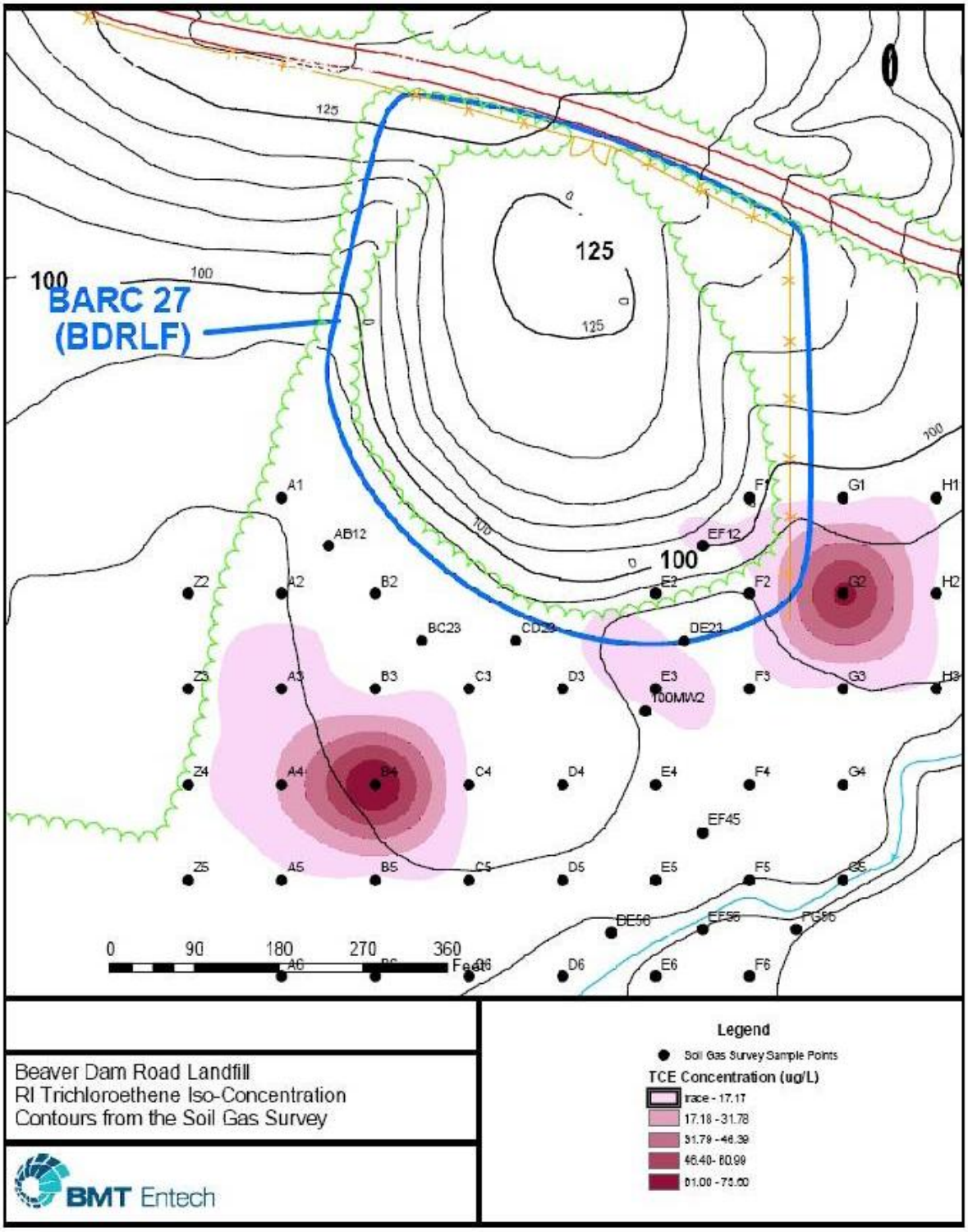

Figure 14 Soil gas survey results TCE distribution.

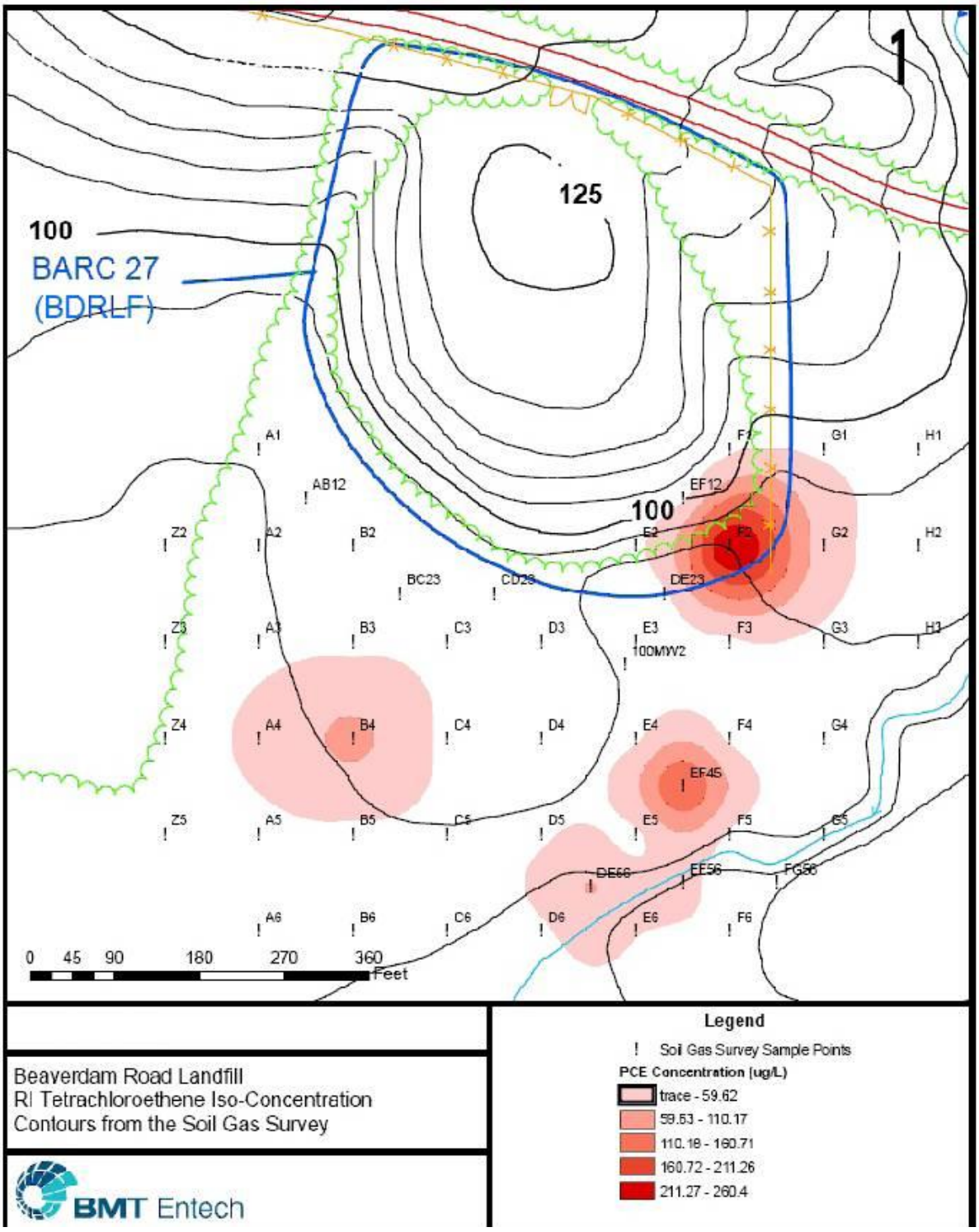

Figure 15 Soil gas survey results PCE distribution.

4.1.2 Soil

Although parameters related to site soil were measured in the groundwater for all monitoring events, actual soil sampling and analysis only occurred for the RI in 2004. During this time, soils were sampled from the same 20 borings used to collect ground water. The soil testing was meant to further delineate areas of suspected contamination, and to assist in selection of additional monitoring well locations. The locations for the borings were determined by the soil gas survey results which BMT Entech interpreted to show two peak areas to the Southeast and Southwest of the landfill.

4.1.2.1 Surface Soil

Surface samples taken from the top 6 in and subsurface samples representing aquifer soils were taken. The details of surface soil sampling are presented in the RI section 3.6.1 (BMT Entech 2008b). Samples were collocated with the geoprobe soil borings. Samples for VOCs were collected by placing the soil directly into a 4oz soil jar with zero headspace. Soil for the remaining analyses was composited in stainless steel bowl before containerizing.

The VOCs methylene chloride, styrene, and TCE were detected in surface soil. Methylene chloride was found in 11 of 20 samples, but all below the reporting limit leading BMT Entech to conclude that it was probably a laboratory contaminant. Styrene was detected 3 times and TCE 2. Both locations B17 and B18 where TCE was detected correlate with a TCE hotspot indicated in both the soil gas survey (Figure 12) and the RI groundwater sampling (Figure 23). BD17 and BD18 are the same locations as RI-GW17 and RI-GW18 shown in Figure 23. These same locations showed subsurface TCE too. The styrene was found in B18 and B20 which also correlate well with this TCE hotspot

and B2 which is in the vicinity of the other TCE hotspot to the southwest. None of the VOCs detected exceeded their USEPA Region 3 residential soil RBC or ecological SSSVs. No SVOCs or pesticides were detected above allowable levels.

The metals aluminum, antimony, arsenic, iron, manganese, and thallium were all detected above their residential soil RBCs. However statistical analysis showed no significant difference between BDRLF and background data sets for Beltsville Research Center. Due to the importance of iron for degradation of chlorinated solvents, its spatial variability at the site is presented in Figure 16. The range of surface iron was 21,700 mg kg^{-1} to 6700 mg kg^{-1} for BD-B14 and BD-20 respectively (Table A-2). Total organic carbon was detected in 15 of 20 samples ranging from 738 to 20,100 mg kg^{-1}. Soil pH ranged from 4.5 to 6.2, with an average of 5.05.

4.1.2.2 Subsurface Soils

The subsurface soil samples were taken in the same way as the surface soils being managed differently for the VOC analysis and the other tests. In addition, samples were scanned with a photo-ionization detector (PID) to assist in the sample selection. The greatest depth of collection was 16 BGS. Samples were collected and analyzed based on the methods presented in Table 12. Because ARARs for subsurface soil are not available BMT Entech using the USEPA's soil-to-groundwater Soil Screening Levels (SSLs) with a dilution attenuation factor (DAF) of 20 (USEPA 1995). TCE was detected in 5 out of 20 samples. The maximum concentration of 669 µg kg^{-1} was detected in sample BD-B17, which corresponds well with the other soil gas survey and surface sampling. TCE was also detected in the adjacent soil boring BD-B18 at 30.2 µg kg^{-1}. BMT Entech states that this represents the eastern edge of the soil gas hotspot. No further interpretation of

the remaining sites with TCE was made. Other VOCs were detected, but they were considered laboratory contaminants. TCE was the only contaminant detected above its soil DAF20 SSL of 0.26 µg kg^{-1}. There were no exceedances of DAF20 SSLs for SVOCs or pesticides. Figure 16 displays spatial distribution of subsurface iron ranging from 40,400 mg kg^{-1} for BD-B11 to 518 mg $kg^{-1}$for BD-B17 (Table A-2).

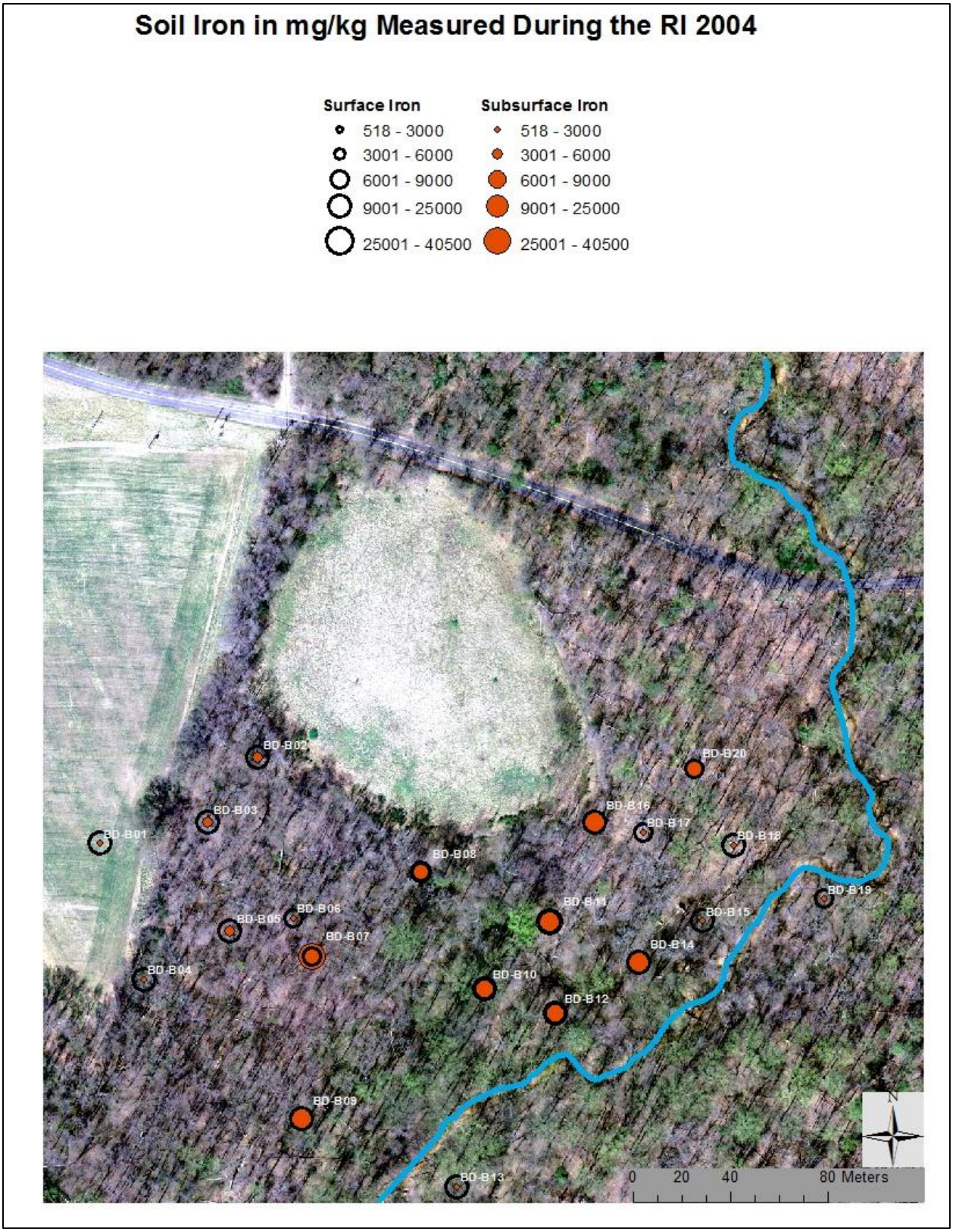

Figure 16 Spatial Distribtution of Soil Iron Measured during the RI 2004.

4.1.2.3 Soil Conductivity

In addition to soil sampling, BMT Entech used conductivity probing to assess the lithology and continuity of clay layers downgradient from the landfill. Conductivity logging was conducted at 31 locations and was meant to assist in the placement of further monitoring wells. As the name suggests, conductivity probing measures the electrical conductivity of the subsurface. The probing indicated that the floodplain soils around the landfill are a mix of discontinuous sand, silt, and clay lenses. From the tip of the landfill south toward the stream channel, the total amount of sand, number of sand lenses, and the thickness of individual sand and gravel units increases meaning that the hydraulic conductivity closer to the stream is likely greater than close to the landfill. A low-permeability clay unit from approximately 25 feet BGS to about 40 feet BGS was detected and confirmed by the well drilling and believed to be the Arundel formation which is known to be 100 feet and greater in this region.

4.1.3 Surface Water and Sediment

To date, BMT Entech has monitored surface water on four occasions. The first two monitoring events included collocated sediment samples, but none of the sediment samples contained significant contaminant levels. The first monitoring event coincided with the SSP in January of 1999. During this event three locations were tested in the creek and two in the wetland to the southwest of the landfill (Figure 1). No chlorinated solvents were detected. The next monitoring event was in January 2004 for the RI. Five locations along the creek were sampled and one in Beaverdam Creek. Three of the five in the creek showed detectable levels of TCE though none above the MCL (Figure 17). In March 2011, BMT Entech sampled four locations in the unnamed creek. The two

southern most points showed decreased levels of TCE from the RI of 0.46 and 0.3 μg L^{-1}. The May 2012 sampling showed no detectable TCE in surface water suggesting that negligible TCE is reaching the creek at this time. The RI sampling showed that no TCE was making it to Beaverdam Creek reaffirming the conclusion in the RI that surface water contamination from the BDRLF is not a human or ecological health risk.

Interpreting the surface water data would be facilitated by additional data about stream volume at the time of measurement, which could be easily estimated by the water depth as long as long as sampling locations are fixed. The last two measurements were made in the same locations, but the previous two were made at different points along the creek further complicating interpretation. Assuming equal water volumes in the creek at the time of each measurement the data may be interpreted as follows. TCE had not begun to enter the creek in 1999, but by 2004 the high concentrations around MW6 were emptying into the creek. By 2011, the initial plume had begun to dissipate as most of the TCE associated with the plume had already exited the site via the creek. Regardless of the data interpretation, TCE levels in the creek have never exceeded the EPA MCL. Therefore, the application of the biowall 50 to 100 feet from the creek is not warranted as the surface water is not a source of contamination downstream. In the future, it is advised that the measurement points in the stream remain the same and that stream depth at the point of measurement is made to assist data interpretation.

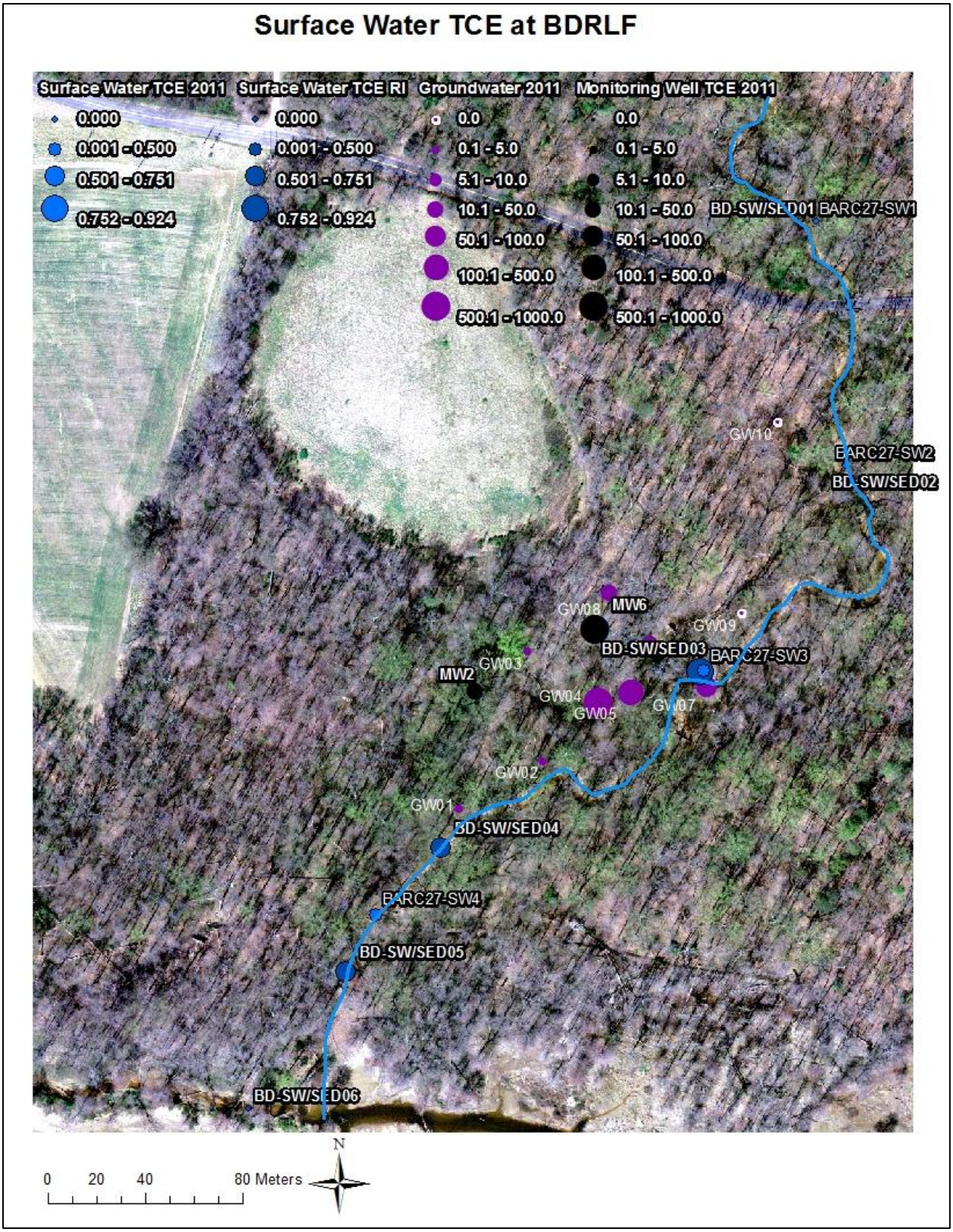

Figure 17 Surface water monitoring at BDRLF in relation to groundwater contamination.

4.1.4 Groundwater

BMT Entech collected data on groundwater contamination starting in 1997 with MW1 through MW4. The purpose of this sampling event was to evaluate existing wells and collect data for future site planning and risk screening. These wells were sampled once more in January 1999 for the SSP before the RI in 2004. Having convinced the USEPA that more study was necessary with the SSP, BMT Entech installed and sampled MW5 through MW9 for the RI in January 2004. From August 2004 to May 2012, all the wells were sampled eight additional times except for MW2 and MW6 which were sampled an added time in March 2011. Three times between 1999 and 2011, temporary groundwater sampling wells were used to test for groundwater contaminants. These monitoring events occurred January 1999, January 2004, and March 2011 coinciding with monitoring well sampling. These data are presented in spatial context in the following three maps Figure 22, Figure 23, and Figure 24.

The primary contaminants of concern compelling the remedial action at BDRLF are CAHs. Therefore, these are the primary data presented here even though low levels of other VOCs, SVOCs, and pesticides have been found at the site. Site iron data is presented and interpreted however due to the possible importance of reactive iron compounds in degradation of CAHs. CAH levels for all the monitoring wells between 1997 and 2011 are displayed in Table A-6 of Appendix A. As shown in Table A-6 b and f, only MW2 and MW6 have shown TCE levels consistently above MCL since 2004. Figure 19 and Figure 20 show temporal change in TCE concentrations within MW2 and MW6 respectively. Figure 19 shows that TCE concentrations in MW2 have generally declined despite for a local peak in August of 2004. Figure 20 shows that MW6 also saw

a localized maximum in August 2004 and then a general decline until March 2011 when the concentration shot up from 0 to 530 μg L^{-1}.

BMT Entech states that this indicates continued release from the landfill, but this is not supported by the site data. The TCE found in MW6 in March 2011 would have exited the landfill 45 years prior assuming no retardation, the flow direction shown in Figure 2, and a seepage velocity of 1.34 m yr^{-1} (Table 2). The distance between MW6 and the closest part of the landfill boundary indicated in Figure 18 is 60 m. The water from GW5 15 m southeast from MW6 along the flow path shown in Figure 18 would have exited the landfill 60 years prior. This interpretation suggests an older release for the TCE observed at the site. Knowing that TCE has been entering the surface water at the site since at least 2004 (BMT Entech 2008b), I estimate that TCE has been leaking from the landfill since the mid-1940s soon after its creation. There is no clear evidence for a more recent release of TCE from the landfill.

The most recent possible release of TCE shown by the data is around 34 years assuming RI-GW17 is in a region with seepage velocity close to MW6 (Figure 18). The actual release may be closer to 50 years if the hydraulic conductivity of the aquifer in this region is lower than around MW6. RI-GW16 upgradient in the general flow path of RI-GW7 has TCE at 0.114 μg L^{-1} suggesting no more recent releases of TCE. I have annotated Figure 18 with red lines indicating flow direction and red boxes highlighting noteworthy spatial and temporal trends.

Box 1 of Figure 18 shows that within that general vicinity new TCE releases are not occurring. Obviously these points are not within the immediate flow path of each other and there is 5 m of separation between the points. It is possible that the

contamination at the site is localized enough to have missed the 2004 and 2011 measurements. This highlights the need to maintain the same sampling points over time to allow for accurate temporal analysis of site data. The conclusion regarding this cluster of points is that TCE has not continued to exit the landfill through this region. SSP-GW4 had the highest ever recorded TCE concentration at the site of 810 µg L^{-1}. GW04 measured 12 years later is within the immediate flow path of SSP-GW4 and showed the highest recorded TCE concentration for this sampling event with 730 µg L^{-1}. At a seepage velocity of 1.34 m yr^{-1} the TCE in SSP-GW4, would take 26 years to reach GW04. Therefore, after 12 years this localized mass of contamination remains on the site roughly in between the two points.

Box 2 shows that in 2004 at RI-GW14 TCE was not found while in 2011 at GW05, 460 µg L^{-1} was detected 5 m downgradient. The GW05 point is 80 m from the tip of the landfill and at a flow rate of 1.34 m yr^{-1} this TCE would have left the landfill in the early 1950s. Again, this provides evidence for an older contamination event sometime between the mid-1940s and early 1950s.

Box 4 shows that significant TCE releases have not occurred in this region for the duration of observation. However, SSP–GW8 and SSP-GW9 show that even in 1999 detectable levels of TCE of 0.83 µg L^{-1} and 4.5 µg L^{-1} were present despite the low seepage velocity of 0.09 µg L^{-1} found in MW2 and the 100 m to 115 m distance from the landfill. Even at the highest seepage velocity of 1.34 m yr^{-1} it would have taken 75 to 86 years to reach this point from the landfill with the exact figure depending on the route taken. This suggests an alternative origin for the TCE. One possibility is the PCE soil gas hotspot 298 feet south of the landfill shown in Figure 15 and Figure 12 point EF45 or

the TCE hotspot located 256 feet south-southwest of the landfill shown in Figure 14. The first spot is the most probable source considering its proximity to the groundwater points. If the PCE hotspot is the source of the TCE found in box 4 and SSP-GW9, then it strongly suggests that PCE is being reduced to TCE. The presence of 0.36 μg L^{-1} of VC in 1999 at SSP–GW8 shows that reducing conditions sufficient enough to generate VC from PCE or TCE are present indicating that the TCE could have come from the PCE hotspot.

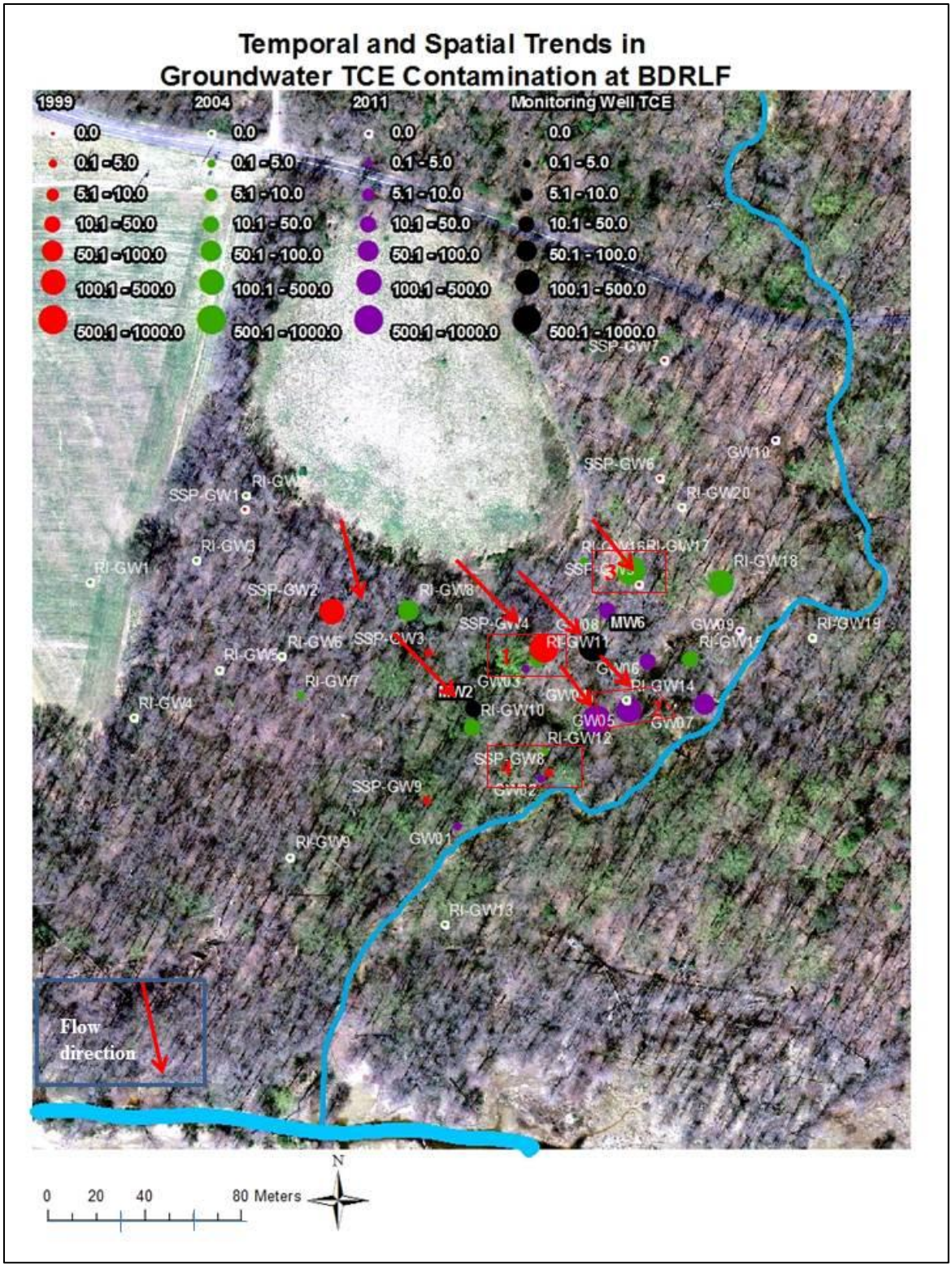

Figure 18 Spatial and temporal trends in TCE concentrations in the groundwater at BDRLF.

The peak in TCE concentrations for MW2 and MW6 in August 2004 highlights the potential seasonality of groundwater concentrations wherein samples taken during the end of the summer when the aquifer volume is at its lowest will show higher TCE concentrations. This poses a problem in interpreting the site data which can be addressed a number of ways. For one, measurements can be made in the same month every year to account for seasonal variability in precipitation and more importantly evapotranspiration, which is at its greatest in the summer months in the midatlantic region of the United States. In addition, the depth to water table can be noted at each monitoring well at the time of sampling to get a sense for the overall aquifer volume. It might be possible to estimate changes in volume in the aquifer based on changes in the potentiometric surface of the aquifer if enough monitoring wells are sampled. By accounting for seasonal changes in aquifer volumes in these ways, a more accurate interpretation of TCE contamination at this site and others could be made.

The constant presence of *cis*-DCE in MW2 suggests a greater level of reductive dechlorination has and continues to occur there than in MW6 which first showed *cis*-DCE above the MCL in April 2008. This may be partly attributable to the greater residence time around MW2 which stems from the one order of magnitude lower seepage velocity (Table 2). The recent appearance of *cis*-DCE in MW6 may indicate localized changes in the soil microbiota permitting biological reductive dechlorination or simply more reducing conditions. The presence of *cis*-DCE in MW2 and MW6 and of 1,1-DCE in MW6 shows that reductive dechlorination is occurring at the site. A possible reason for the observed degradation byproducts is geochemical degradation spurred by reactive iron in the site soil. Dong et al. (2008) found that abiotic reductive dechlorination

happens much more slowly than biotic, which matches well with the higher levels of *cis*-DCE found in MW2 where the residence time for TCE is much higher than in MW6.

The other seven wells have shown TCE levels below detection limits for the entire eight year period or below the MCL for TCE. Values of 0 indicate levels below the detection limit which was 0.17 µg L^{-1} (Table A-6). During the SSP, MW1 showed TCE levels at 45 µg L^{-1} exceeding the MCL, but showed no detectable TCE thereafter.

Because reactive iron species can reduce CAHs I have presented the spatial distribution of iron in the groundwater throughout time to assess whether a positive spatial link can be made between iron and degradation at the site. Figure 21 shows the distribution of iron sampled from the geoprobe wells at the time of boring. The samples were analyzed based on the Target Analyte List (TAL) using the method listed in Table 12. The range of iron values was 18200 µg L^{-1} to 665000 µg L^{-1} (Table A-7) whereas for the monitoring wells sampled at the same time it was 3780 µg L^{-1} to 22100 µg L^{-1} (Table A-8), approximately one order of magnitude lower. Because the monitoring wells had so much lower values it was difficult to clearly present them on the same map so these values are excluded from Figure 21. The same phenomenon is seen in the 1997 monitoring well iron data (Table A-9). This suggests that the well packing of sand and gravel and the well screen may be reducing the dissolved and particulate iron in the water yielding an inaccurate measure of total and reactive iron.

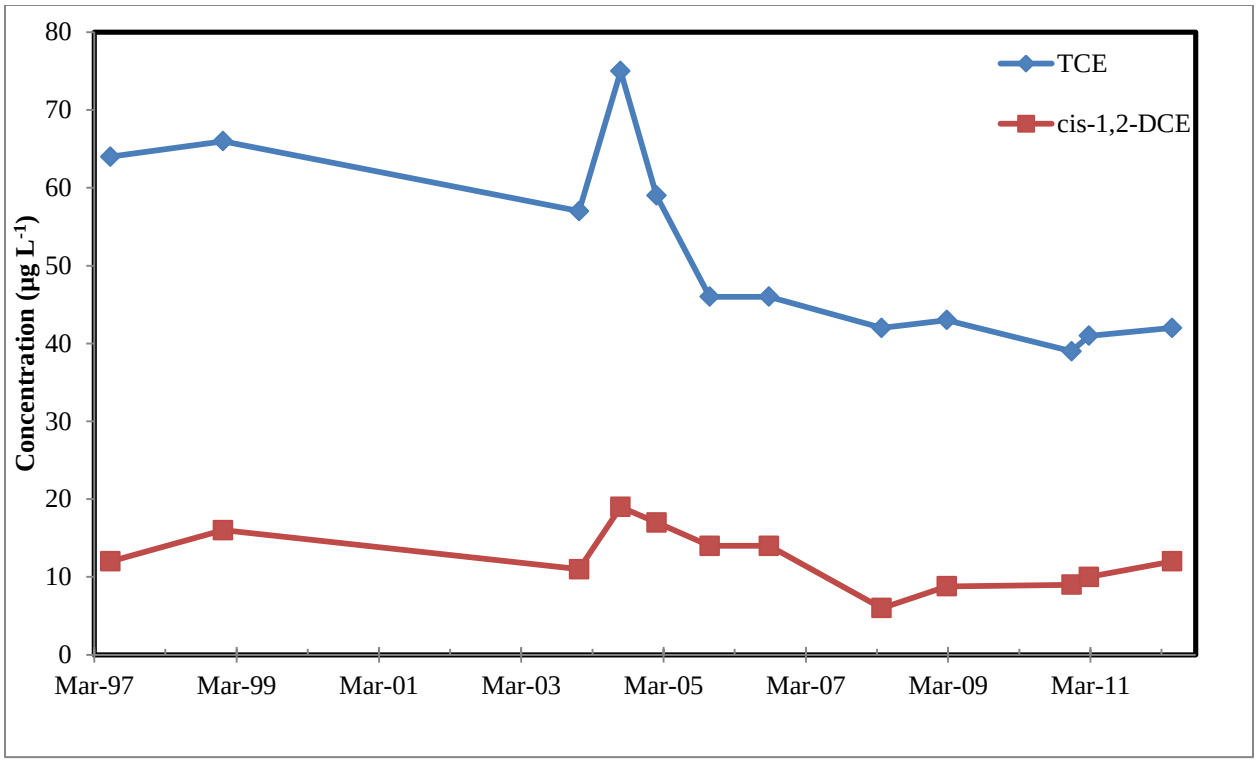

Figure 19 MW2 TCE and cis-1,2-DCE concentrations over 15 years.

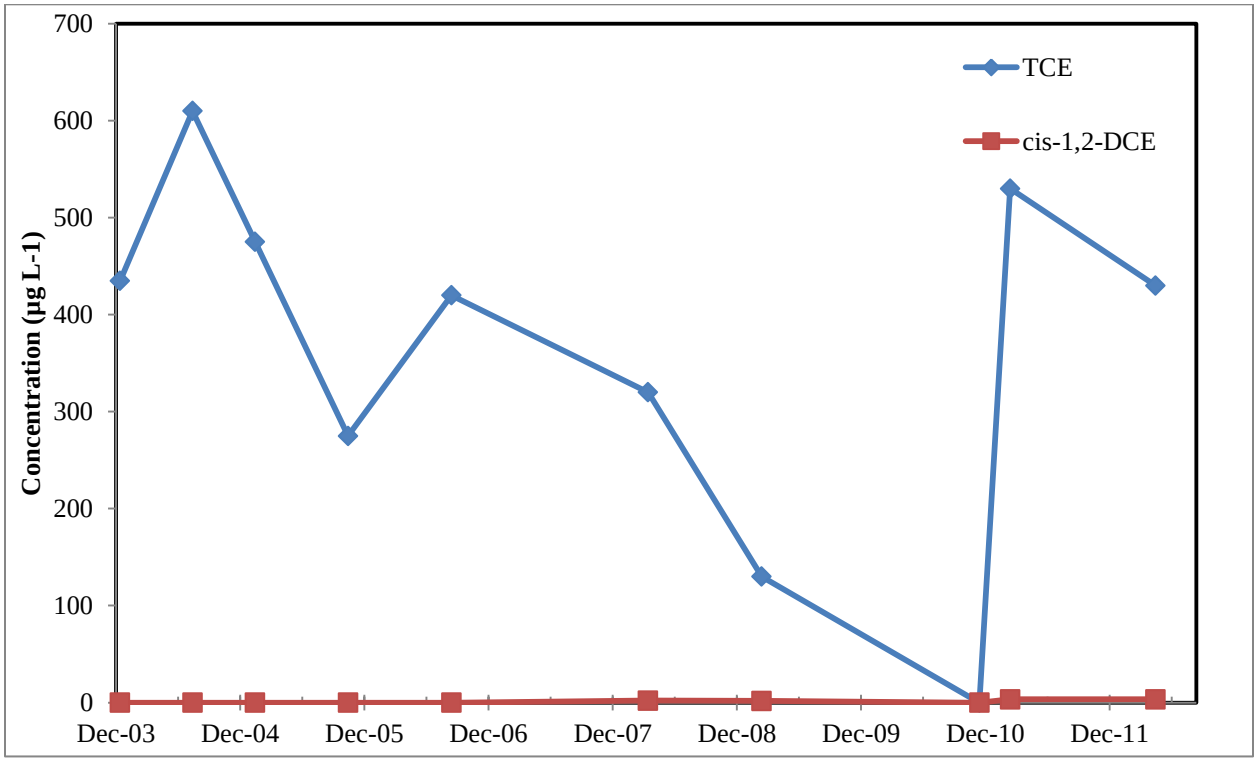

Figure 20 MW6 TCE and cis-1,2-DCE concentrations over 8.5 years.

Nevertheless, the 2004 monitoring well sampling showed the presence of ferrous iron Fe(II) in all the wells except MW2. For instance, MW4 from which water was extracted for the batch experiment in 2011 showed 5.88 mg Fe(II) L^{-1}. MW6, the permanent well with the highest and most consistent TCE contamination showed the second highest levels of Fe(II) at 6.8 mg L^{-1} (Table A-8). Ferrous iron was measured using a Horiba U-10 Water Quality Checker as part of the geochemical characterization of the site. Considering that this may be an order of magnitude underestimate of Fe(II), it is possible that the site has considerable amounts of reactive iron which could promote the biogeochemical degradation of CAHs. When assessing the potential of natural attenuation of CAHs in groundwater at future sites, it should be noted that the amount of reactive iron measured in screened wells may be appreciably lower than what is actually present in the groundwater.

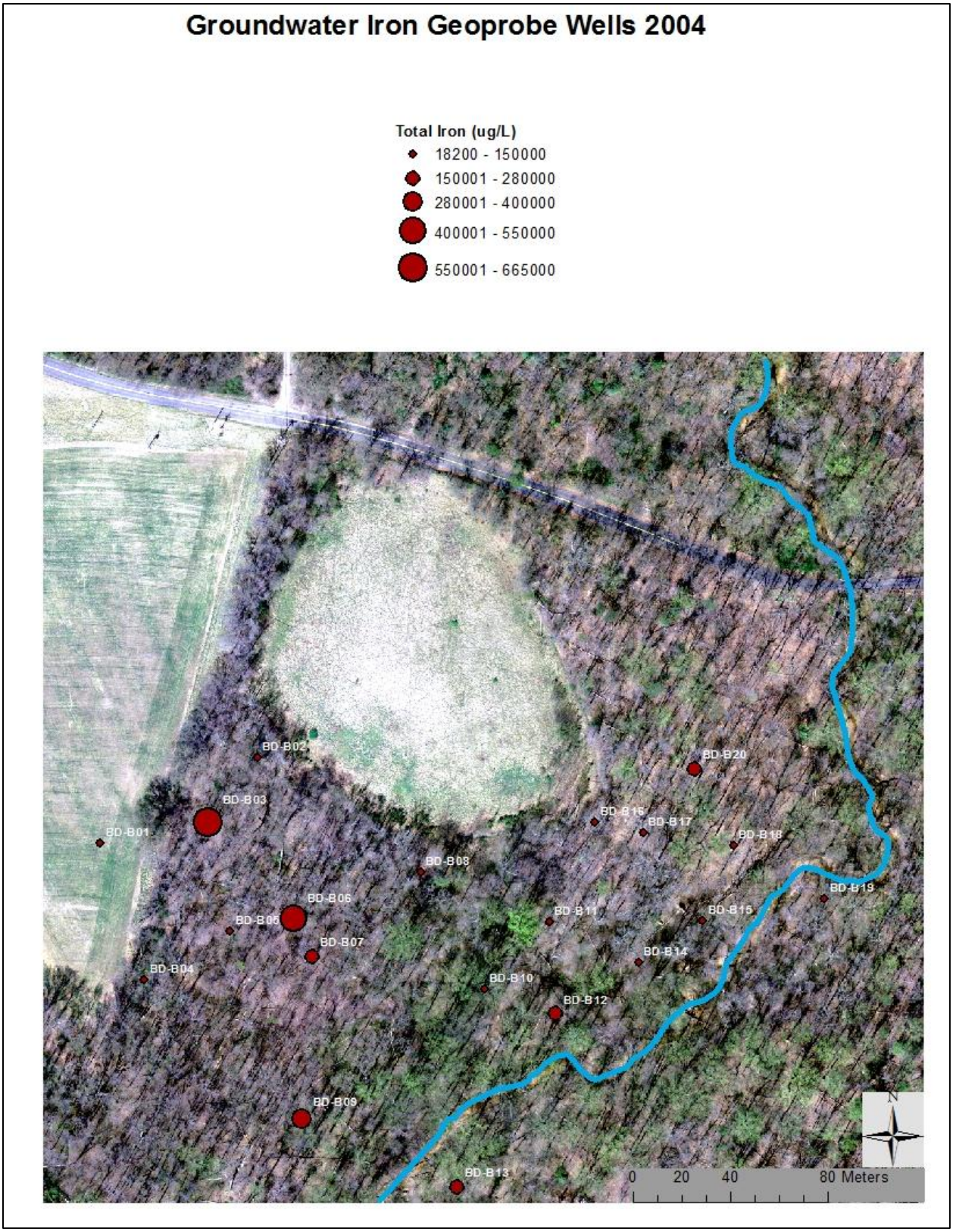

Figure 21 Distribution of iron in groundwater sampled by geoprobe in January 2004.

4.1.4.1 Conclusions

1. Establish clear transects along the groundwater flow path and monitor them over time in the same exact locations to establish temporal and spatial trends in the data.

2. Account for the effects of aquifer volume on the TCE concentrations measured by gaging depth to the water table at each sampling time.

3. More data on spatial variations in groundwater flow at the site would permit more accurate interpretation of the groundwater data.

4. Do not proceed with the biowall unless it is proven that the landfill is or will continue to release TCE.

5. When assessing the potential of natural attenuation of CAHs in groundwater at future sites, it should be noted that the amount of total and ferrous iron measured in screened wells may be appreciably lower than what is actually present in the groundwater.

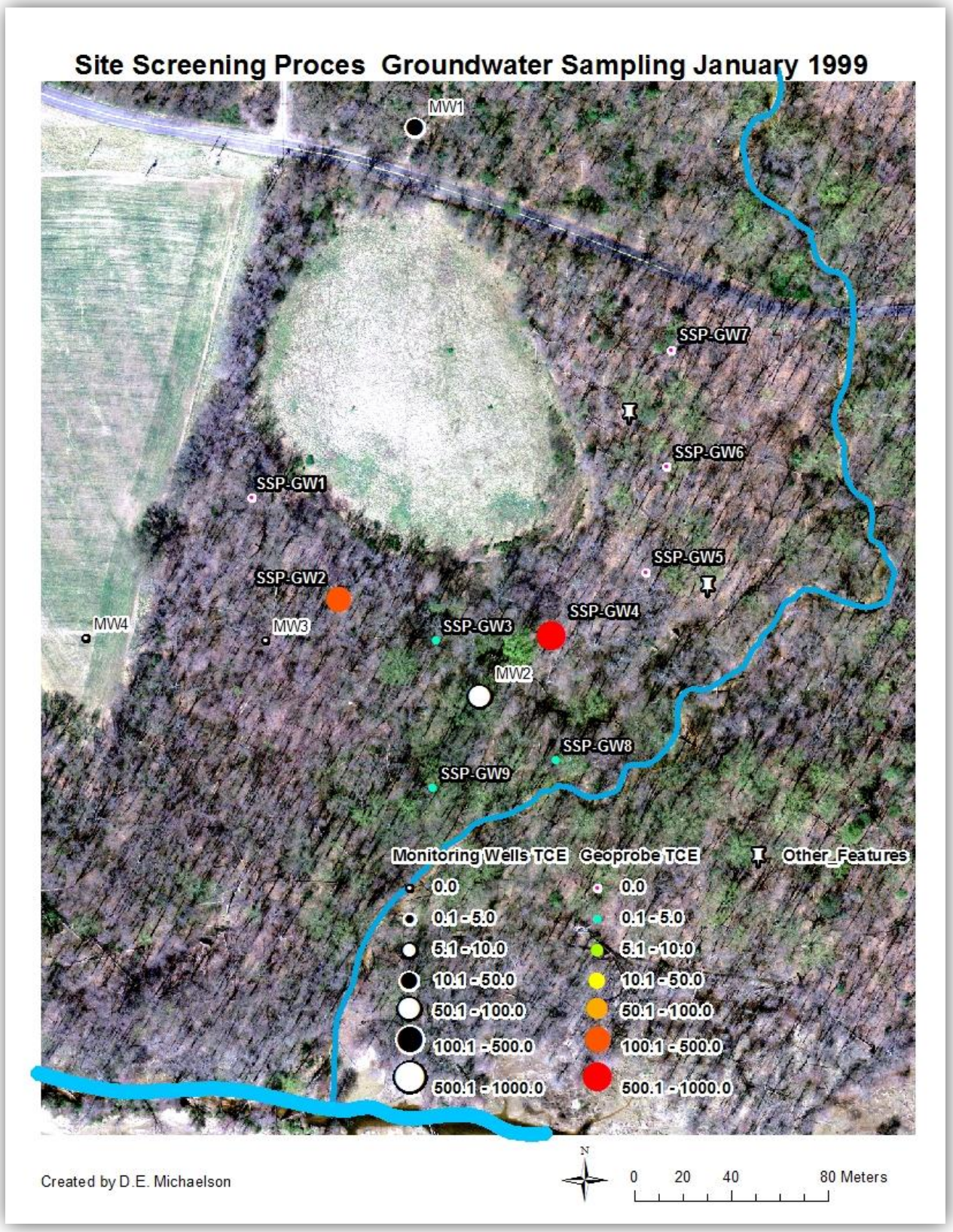

Figure 22 Site screening process groundwater monitoring 1999.

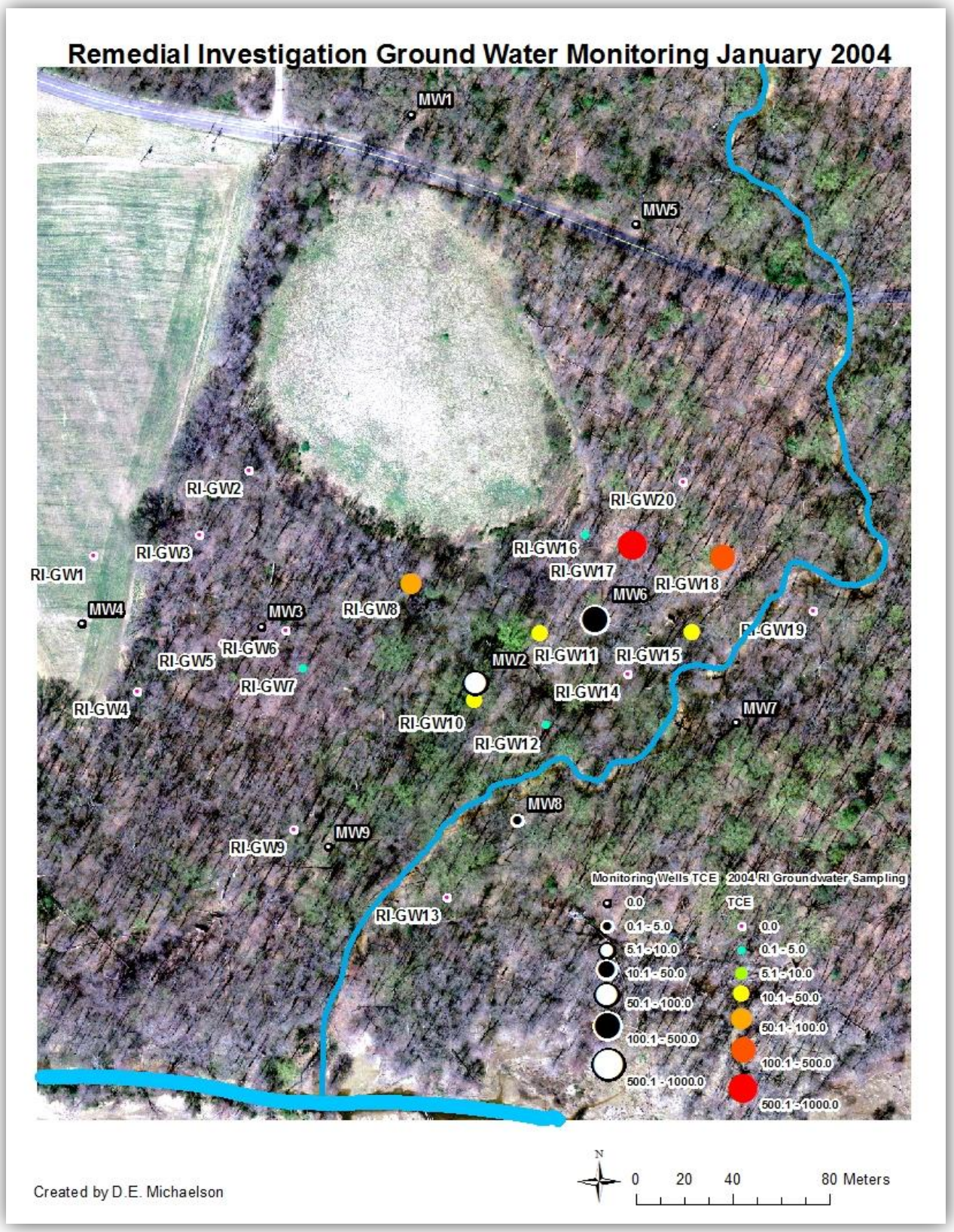

Figure 23 Remedial Investigation groundwater monitoring January 2004.

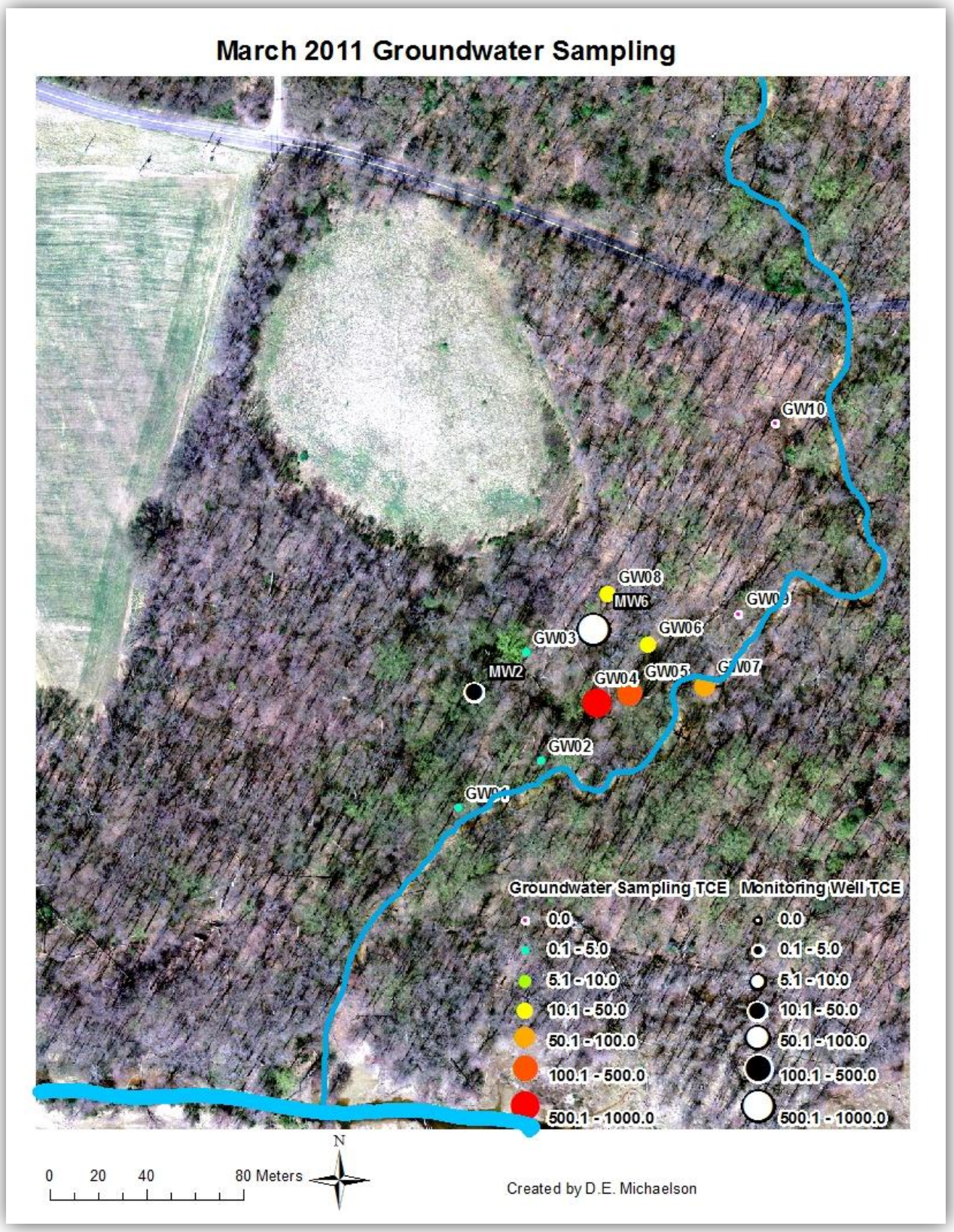

Figure 24 March 2011 sampling event in preparation for biowall construction.

4.1.5 Quality and Interpretation of Site Data

The accuracy of the data is questionable in some instances. For example, the December 2010 sampling which showed 0 TCE in the groundwater from MW6 followed by a spike back up to 530 µg L^{-1} in March 2011. BMT Entech explained this as a sign of continued release from the landfill, but it is also possible that the non-detect measurement was a lab or collection error. Alternatively it may have resulted from seasonal variations in the aquifer volume. Regardless, I showed in the section on groundwater that the TCE detected in March 2011 would have been released from the landfill 45 years prior anyway, nullifying the point that the spike represents continued release of TCE.

On multiple occasions during the RI, BMT Entech either incompletely presented or misrepresented site data. For instance, the 1999 Site Screening Process indicated that background MW1 had a TCE concentration of 45 µg L^{-1}(Table A-6). This observation was never mentioned in the text of the document or given an explanation of any kind. TCE-contaminated groundwater upgradient of the landfill does not match with the reported groundwater flow direction determined by BMT Entech in either the baseline groundwater sampling (1997) or the remedial investigation (2004). This suggests a contamination source upgradient of the landfill or a measurement error. The later possibility calls all of the site data into question.

The complete SSP analytical results are never presented and the only semi-complete representation of the data appears in the RI within Figure 1.5. This figure contains 9 geoprobe locations, but skips label GW9, confusing data interpretation. It contains no metals data. In this document the sampling points are labeled GW1 through GW9. According to the RI, the SSP included surface soil, subsurface soil, surface water

and sediment sample analysis for TCL VOCs , SVOCs , OC pesticides, PCB s , and TAL metals. Groundwater samples were only analyzed for TCL VOCs and TAL metals. None of this data is presented in the RI appendix and there was not a separate presentation of the SSP anywhere based on a personal communication with BMT Entech.

Neither BMT Entech nor Tidewater Inc. the consulting firm responsible for the soil gas survey, present the soil gas data in full. For example, they fail to mention the PCE high point of 1054. 68 µg L^{-1} at EF45 and misrepresent it as shown in Figure 15. BMT Entech does not address the co-occurrence of chlorinated ethanes and ethenes and multiple degradation products at the three most contaminated measurement locations. Moreover, they assume that all the contamination at the site comes from the landfill when simple distance measurements show that multiple contaminant areas at the site could not have originated in the landfill based on measured groundwater velocities.

The distances to the soil gas contaminant hotspots B4 and G2 are incorrectly calculated as 140 and 120 feet when calculation using GIS showed they were 256 feet and 160 feet. G2 is only the TCE hotspot. The PCE hotspot which is lumped with that of TCE is actually at F2, 115 ft upgradient of G2 (Figure 12). An example of misrepresentation of site data is seen in Figure 14 and Figure 15 in which BMT Entech use a model which assumes the soil gas hotspots as the contaminant origin with contaminant concentrations increasing in concentric circles of equal contamination. This does not make sense when considering groundwater flow direction or even with the assumption that the contamination originates in the landfill.

On page 83 of the RI, BMT Entech erroneously states that BD-B15 is on the east side of the unnamed tributary and that the presence of PCE, TCE, *cis*-DCE, *trans*-DCE,

and VC on the eastern side of the tributary indicates that VOCs in the shallow groundwater are migrating past the creek in the southerly direction. As seen in Figure 23, BD-B15 is approximately 15 m west of the unnamed tributary, rendering the BMT Entech statement incorrect.

There was an apparent error in the spatial representation of all data points in the RI and FS as seen in the change in MW orientation in the top two images of Figure 25. The one on the left represents the placement of the monitoring wells throughout the remedial process. This orientation remained until March 2011 when it appears an error in the GPS coordinates for the monitoring wells was discovered and new coordinates were taken as reflected in the top right image. The bottom images show the BMT Entech map and one used in this document that both employ an aerial photograph as the base layer. The points align well. This error in GPS coordinates may be responsible for the miscalculations made in the RI and calls into question the other data points with spatial reference information.

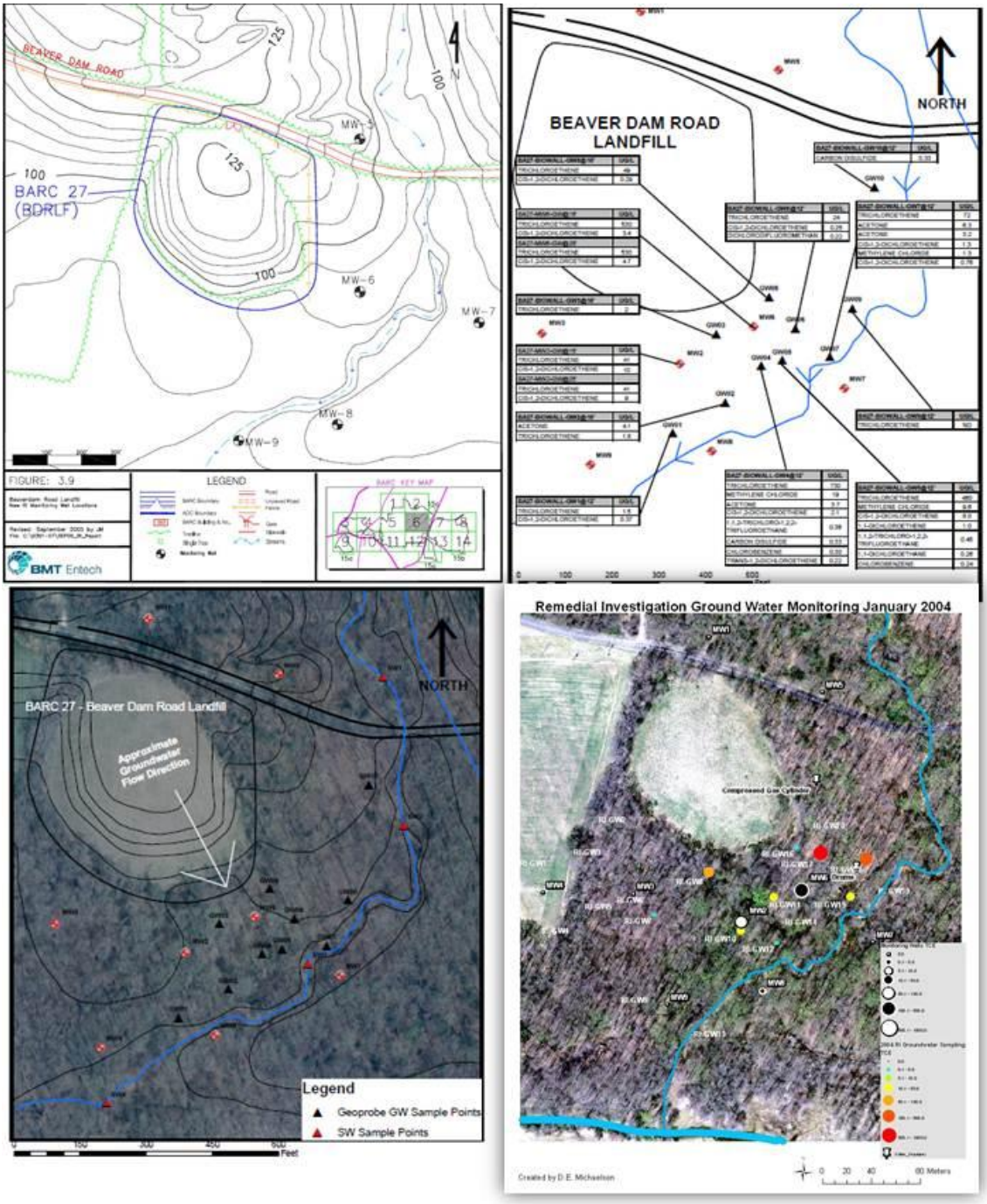

Figure 25 Spatial representation error and corrected map in comparison to those used here.

4.2 Assessing the Biowall Material

The batch study was originally intended as a standalone master's project with the purpose of advising the design of the BDRLF biowall and providing future biowall projects with useful information. The original intentions remain and are addressed in the following section with the addition of an assessment of the natural attenuation potential of the site soil and groundwater. The results presented are preliminary and will be replicated and expanded upon in forthcoming research.

4.2.1 Background Data

To inform the experimental design of the lab study and field application of the biowall, I derived a range of data for the biowall mixes. These data include measured values of hydraulic conductivity for the biowall media and a comparison to literature values for organic material similar to the biowall material plus the site soil (Table 13 and Table 14 respectively). These data show little difference in hydraulic conductivity between the two unamended biowall media (Table 13) and that the conductivity of the biowall media is slightly above or about the same as the site soil (Table 14).

Table 13 Measured hydraulic conductivities (K) of biowall mixes

Description	K range (cm/sec)	Average K (cm/sec)
MX1 (M1/C1)	0.000060-0.00010	0.000081
MX2 (M5/C1)	0.00006-0.000063	0.000062

Table 14 Hydraulic conductivities of organic media and site soil for comparison to biowall media

Source & Description	Hydraulic Conductivity cm s^{-1}	Method
Mulch from Unv. Central Florida Extension	0.09	ASTM D2434-68
100% mulch from Ahmad et al. (2007)	0.0015	ASTM D5084
70%:30% mulch:pea gravel (vol:vol) mulch from Ahmad et al. (2007)	0.0021	ASTM D5084
50%:50% mulch:pea gravel (vol:vol) mulch from Ahmad et al. (2007)	0.00349	ASTM D5084
BMT Entech BARC 27 aquifer	$6.88x10^{-6}$ to $1.02x10^{-4}$	Slug test

Background nutrient analyses on the compost used in the study were made by the PENN State Analytical Laboratory. Bulk densities of the individual biowall media constituents and final mixes were made in house. I also measured the reduction in volume for the biowall media after mixing. MX1 experienced an average volume reduction of 13% (n=4, SD=5.72) and MX2 experienced an average volume reduction of 26 (n=3, SD=4.04).

Total carbon of the compost was measured by the PENN State lab, but additional carbon measurements of the wood mulch and final mixes were made in-house using a loss on combustion approach. This measurement was used to estimate the fraction of organic carbon in each media required for the creation of a mass balance and determination of the partitioning coefficient (k_d) for each media.

The mass balance was created to estimate partitioning between the gas, water, and solid phases within the microcosms. This information was necessary to provide an estimation of expected concentrations of TCE in each phase. Table 15 and

Table 16 display the background data needed for formulation of the mass balance and the partitioning of TCE at equilibrium respectively. Table 17 shows the data needed for calculation of f_{oc} in MX1 and MX2 and indicates the calculated values.

Table 15 Background data for mass balances of TCE partitioning in unamended mixes 1 and 2

Treatment	Vol solids (L)	Volume water (L)	Volume air (L)	foc^{+}	Kd	TCE concentration (mg L^{-1})	Weight TCE (mg)	Weight solids (g)
MX1	0.5	0.30	0.4	0.056	0.001	0.1	0.03	545
MX2	0.5	0.30	0.35	0.072	0.002	0.1	0.03	530

Table 16 Partitioning of TCE in mixes 1 and 2 at 10ºC assuming equilibrium and 1 atm of pressure

Treatment	TCE concentration air (mol L^{-1})	TCE concentration water (mol L^{-1})	TCE mass sorbed to solids (moles)	fair	fwater	fsolids
MX1	3.67E-08	2.30E-07	1.45E-07	0.06	0.30	0.63
MX2	3.13E-08	1.96E-07	1.57E-07	0.05	0.26	0.69

Table 17 Fraction carbon measured by loss on ignition at 550 °C

Sample	Replicate	Organic matter (g)	Organic carbon (g)	Fraction organic carbon (g g^{-1})	Average foc (g)
MX1	A	24.4	12.2	0.069	0.056
	B	16.1	8.05	0.042	
	C	22.1	11.05	0.058	
MX2	A	19.1	9.55	0.084	0.072
	B	18.6	9.3	0.066	
	C	20.1	10.05	0.064	

4.2.2 Mass Balance

The quality assurance mass balance showed that the average mass of TCE in the sand jars was 21.76 µg after a one-week equilibration period with a standard deviation of 4 and sample size of 3. This means that an average of 8.23 µg or 27.4% of the original TCE mass was not accounted for after five days assuming no adsorption. It could be that the assumption of no adsorption is flawed and some TCE sorbed to the sand particles or dissolved particles in the groundwater. TCE reduction may have occurred over the period. Losses of TCE due to improper handling during spiking may account for some of the mass, but standard laboratory operating procedures were followed. The headspace did not show any reductive dechlorination byproducts after five days decreasing the likelihood that the mass loss is attributable to microbial reductive dechlorination which produces the expected microbial dechlorination byproducts.

In future studies the hypothesis of initial degradation due to site water can be tested by comparing headspace concentrations after five days using spiked DI water and site groundwater. This will also help to identify if dissolved particles in the site groundwater sorb TCE.

The experimental results fit with the partitioning mass balances almost exactly. For MX1, the distribution of TCE mass between the air, water, and solid phases was projected to be 6%, 30%, and 63%. These same values were found for the average partitioning in the three replicates of MX1. In MX2, the fractionation was higher to the solid phase because of greater total organic carbon. The partitioning was 5% air, 26% water, and 69% solids. The MX2 partitioning was almost identical to the projected distribution.

To calculate partitioning in MX1 and MX2, the first recorded TCE headspace concentration and resultant mass were used to check the mass balance. Consequently, the actual mass used to calculate partitioning was not the 30 µg added, but the mass calculated based on the headspace concentration after five days. In some cases, this mass was almost exactly 30 µg, but in most cases it was higher or lower. This could be caused by variation in the K_d value for the replicates. Assuming a starting mass of 30 µg would require increasing the K_d when masses were below and decreasing the K_d for treatments with masses above the input. This is a real possibility given the heterogeneity of the mixtures. Other explanations include degradation after 5 days and losses due to leaking from the jars both of which would not have to be dealt with for the mass balance, but would have to be considered when calculating total mass removed versus degraded.

4.2.3 Temperature

Although temperature was supposed to be set to 12°C for the duration of the study some modifications were made due to imperfections in the wine coolers and the actual temperatures in the wine coolers varied. The average for cooler 10.2°C (STDEV=2.7) and the average for cooler 2 was 10.04°C (STDEV=2.8). Plots of the temperature over time for coolers 1 and 2 are presented in Appendix C Figure C-1 and Figure C-2.

After 144 days, all the treatments including the soil and sand spikes showed at least 35% average reduction in TCE mass. Figure 26 shows the percent TCE mass reduction overall and by degradation. Total TCE removal is greater than removal via degradation because mass was removed at each sampling point to permit GC-MS analysis. Unless otherwise stated, the removal percentage reported is for degradation rather than total removal.

The greatest average percent removal was for those treatments with ZVI. The greatest percent degradation of 99.15% was for MX1 with the high dose of glycerol and ZVI or 30 ml of glycerol per liter of solids and 100 ml of ZVI per liter of solids. The treatments with glycerol as the only amendment performed the poorest. The lowest level of TCE degradation was 39.5% for MX1 with the high dose of glycerol. MX2 did not experience the high amendment dose, but the second lowest amount of degradation (40.9%) was for MX2 with the low glycerol dose. Both the sand and soil spikes showed significant degradation of 48.4% and 58.1% respectively. These data are presented in tabular form in Table 18. Highlighted items indicate that the jar had to be remade due to leakage. MX1 created higher TCE removal for both baseline and amended treatments. The average removal efficiency for MX1 with no amendments was 75.52% (STDV=19.9%) while for MX2 it was 72.47% (STDV=19.7%).

A number of anomalous results were generated by the glycerol treatments. For example, jar 33 which was the third replicate for the MX2 low glycerol (G10) treatment showed 97.8% removal while the other two replicates showed 29.1% and 0% removal. Jar 21, the second MX2 low glycerol treatment, showed a decrease in TCE by the end of the study, but the amount theoretically removed by sampling was less than the difference between starting and ending masses yielding slightly negative removal efficiency. This is likely due to estimation errors.

Another anomaly related to Jar 21 is the increase in headspace TCE concentrations over time, which eventually returned to around the starting concentration. This jar was not included in calculation of average removal efficiency. Jar 3 which was the first replicate of MX1 with high glycerol (G30) increased and decreased in TCE

concentrations during the study and by the eighth measurement the GC-MS could not get a reading because the device was overrun by CO_2. This jar was not included in the calculation of average removal efficiency. The other two replicates for this treatment deviate severely with removal efficiencies of 5.1% and 78.3%. Jar 36, the last replicate of the soil spike showed much higher removal (98.1%) than the other two treatments with 39.6% and 36.5%.

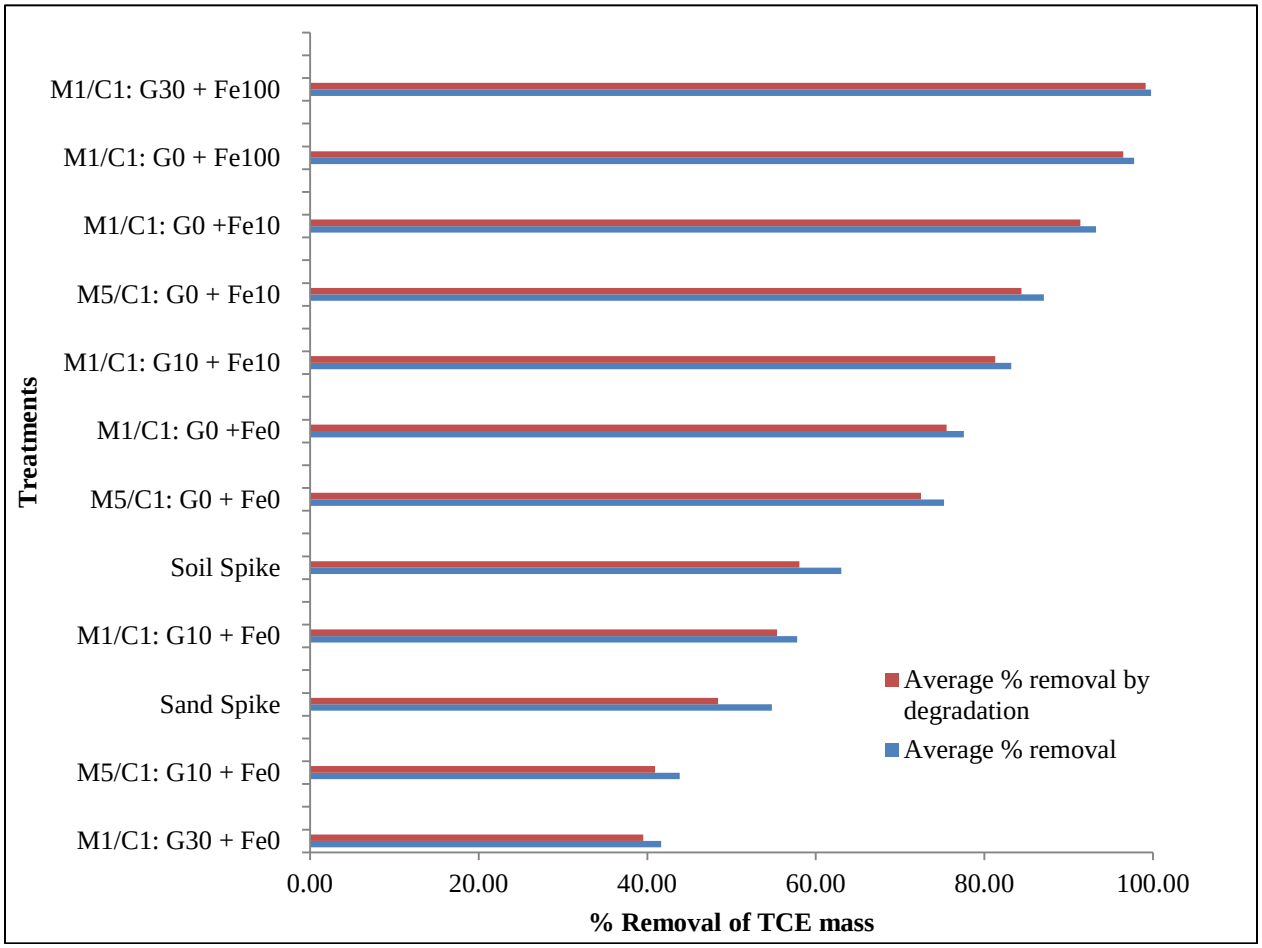

Figure 26 Total mass removed and degraded for the treatments, sand, and soil spikes.

Table 18 Removal efficiency for each treatment in the batch study

Treatment and Rep	Jar #	% removal TCE	Average % removal	% removal via degradation	Average % removal	Standard deviation
Sand Blank R1	0^{-1}	0.0		0.0		
Sand Blank R2	0-2	0.0	0.00	0.0	0.0	0.0
Sand Blank R3	0-3	0.0		0.0		
M1/C1: G0 +Fe0 R1	1	100.0		98.1		
M1/C1: G0 +Fe0 R2	13	69.8	77.57	67.8	75.5	19.9
M1/C1: G0 +Fe0 R3	25	62.9		60.6		
M1/C1: G10 + Fe0 R1	2	43.3		40.8		
M1/C1: G10 + Fe0 R2	14	60.2	57.79	58.2	55.4	13.4
M1/C1: G10 + Fe0 R3	26	69.9		67.2		
M1/C1: G30 + Fe0 R1	3	Error		Error		
M1/C1: G30 + Fe0 R2	15	5.1	41.67	2.1	39.5	52.9
M1/C1: G30 + Fe0 R3	27	78.3		76.9		
M1/C1: G0 +Fe10 R1	4	96.3		93.4		
M1/C1: G0 +Fe10 R2	16	84.4	93.25	82.5	91.4	8.1
M1/C1: G0 +Fe10 R3	28	99.1		98.3		
M1/C1: G0 + Fe100 R1	5	100.0		98.7		
M1/C1: G0 + Fe100 R2	17	96.3	97.76	95.0	96.5	2.0
M1/C1: G0 + Fe100 R3	29	97.0		95.8		
M1/C1: G10 + Fe10 R1	6	100.0		98.1		
M1/C1: G10 + Fe10 R2	18	86.5	83.19	84.9	81.3	18.9
M1/C1: G10 + Fe10 R3	30	63.1		60.9		
M1/C1: G30 + Fe100 R1	7	99.3		99.1		
M1/C1: G30 + Fe100 R2	19	100.0	99.77	99.3	99.2	0.1
M1/C1: G30 + Fe100 R3	31	100.0		99.1		
M5/C1: G0 + Fe0 R1	8	67.6		64.8		
M5/C1: G0 + Fe0 R2	20	60.2	75.20	57.8	72.5	19.7
M5/C1: G0 + Fe0 R3	32	97.9		94.8		
M5/C1: G10 + Fe0 R1	9	29.1		25.6		
M5/C1: G10 + Fe0 R2	21	3.1	43.85	-0.7	40.9	51.0
M5/C1: G10 + Fe0 R3	33	99.4		97.8		
M5/C1: G0 + Fe10 R1	10	87.2		84.5		
M5/C1: G0 + Fe10 R2	22	81.2	87.07	79.0	84.4	5.4
M5/C1: G0 + Fe10 R3	34	92.8		89.7		
Sand Spike R1	11	50.6		44.0		
Sand Spike R2	23	57.6	54.77	51.8	48.4	4.0
Sand Spike R3	35	56.1		49.5		
Soil Spike R1	12	46.1		39.6		
Soil Spike R2	24	43.1	63.02	36.5	58.1	34.7
Soil Spike R3	36	99.9		98.1		

4.2.4 Data Interpretation

The results show a positive correlation between the amount of ZVI added to the biowall mixtures and the amount of TCE degradation. Both lab and field-scale experiments have previously shown that ZVI can significantly decrease groundwater TCE concentrations via reductive dechlorination (Orth and Gillham 1995, Phillips et al. 2010). Tratnyek et al.(2001) found that NOM inhibited TCE reduction by ZVI and Giasuddin et al. (2007) showed that ZVI reacts with DOC possibly decreasing its availability. Additionally, Zhang et al. (2011) found that soil organic matter (SOM) decreased the rate of TCE degradation by nanoparticle ZVI in soil media. In this study however, the data do not indicate that the organic fraction of the biowall media inhibited TCE degradation. This question could be addressed in future experiments by including a ZVI-sand treatment for comparison to the ZVI-biowall media.

Both the sand spike and soil spike showed significant degradation of 48.4% and 58.1% respectively. Being that the concrete sand used in the study is little more than silicon dioxide, the site groundwater must have promoted some level of TCE degradation. The most likely catalyst for degradation is iron. The groundwater used in the batch study came from the vicinity of MW4. BMT Entech collected geochemical data for all the monitoring wells for the RI and found that MW4 had 5.8 mg L^{-1} Fe(II). Fe(II) can act as an electron donor for the reduction of TCE and is a precursor of FeS minerals known to reduce TCE (Shen and Wilson 2007). This may partially explain the measured degradation of TCE in the soil and sand spikes.

It is important to note that the quality assurance mass balance performed on the sand spike showed that after five days only 72.6% of the initial 30 µg of TCE was

detected and that degradation efficiencies were calculated using an average of 21.76 µg rather than 30 µg as a starting TCE mass. If unaccounted for sorption was the reason for the initial decrease in TCE mass, then the stated removal efficiencies for both the sand spike and soil background are accurate. However, if the reason was abiotic degradation, then the removal efficiency would be even higher. This illustrates the need to perform further batch studies assessing the role of sorption to groundwater and soil particles.

The treatments with only glycerol amendment performed the most poorly with the highest glycerol amendment ranking lowest among the treatments (Figure 26). Two of the glycerol treatments showed less average TCE degradation than the sand spike which suggests that the glycerol actually inhibited degradation. The MX1 low glycerol treatment achieved slightly more degradation than the sand spike, but lower than the soil spike. Because of its limited or negative contribution to TCE degradation, crude glycerol is not recommended as a liquid carbon amendment for use with biowalls.

It was initially chosen for its low cost and readily available carbon fraction, but due to cross contamination from industrial byproducts it may have inhibited TCE degradation. A higher grade glycerol could be tested in the future or emulsified vegetable oil, which has been used on several occasions, could be incorporated into future experiments though the cost is greater. Treatments with iron and glycerol still performed better than the non-amended treatments indicating that the iron was able to counteract negative effects of the glycerol.

Five of the jars in the batch study had to be replaced within two weeks of the start. To deal with these failures, we restarted the jars and incorporated them back into the measurement rotation, extending their measurement two weeks longer than the other jars.

Four of the five restarted jars showed greater than 95% TCE degradation. This could be caused by variations in temperature during the study period and indicates that future replication is needed. Another contributing factor is that newly mixed materials were used for the replaced jars which were created with mulch that had aged for a longer period of time than the previous material. More labile carbon could have resulted, spurring the greater removal efficiencies.

Another element belying the need for more replication is that the standard deviation between removal efficiencies for six of the ten treatments was greater than 18%. The two highest standard deviations were for MX1 high glycerol (STDEV=52.9%) and MX2 low glycerol (STDEV=51.0%). The other four high variance treatments showed much lower standard deviations of 18.9%, 19.7%, 19.9% and 34.7%. The restarted samples are partly responsible for the high standard deviations. For example, the two original non-amended MX1 jars showed 69.8% and 62.9% degradation while the replaced jar showed 98.1%.

A similar situation occurred with the third replicate of the soil spikes which showed 98.1% removal efficiency while the other two replicates showed 39.6% and 36.5% removal. In the case of the soil spikes, the original mixture of equal parts of soil from soil bore 6 and 16 had to be supplemented with additional material from soil bore 6. Therefore the higher removal efficiency may be attributed to soil properties of soil bore 6, such as mineralogy or microorganism communities. Future studies may want to investigate the difference in iron mineralogy and microbial communities between the two soil boring or at different locations at the site to see if there is a link between FeS minerals and natural attenuation at the site.

Despite the need for replication of the experimental results, recommendations can still be made from the initial batch study data. Because the cost of ZVI for use in the site biowall would exceed $1 million, unamended MX1 is the best biowall material unless the site soil provides enough degradation as is. This is based on the superior degradation offered by this material compared to MX2 though the difference in degradation is not statistically significant.

4.2.5 Hydrologic Considerations

According to Ahmad et al. (2007) permeable reactive barriers such as the biowall should be more permeable than the surrounding formation to allow for preferential flow of contaminated groundwater to occur. Henry et al. 2008 state that the biowall should be designed to meet or exceed the highest potential seepage velocity at the site. Based on measurements of hydrologic conductivity (K) of the biowall media shown in Table 13 and of the BDRLF groundwater seepage velocity shown in Table 1, one may see that both MX1 and MX2 have slightly lower hydraulic conductivities than the highest measured conductivity of the site soil. MX1 and MX2 had average conductivities of $8x10^{-5}$ and $6.2x10^{-5}$ cm s^{-1} respectively. These values are slightly lower than the highest recorded site hydraulic conductivity of $1.02x10^{-4}$ cm s^{-1}. MX1 which contained 30% compost, 30% mulch, and 40% sand by volume had a higher average K value. Therefore, on grounds of hydraulic conductivity this is the preferred medium.

4.3 Natural attenuation

The USEPA protocol for evaluating the potential for natural attenuation of chlorinated solvents in groundwater systems recommends multiple lines of evidence and

anticipates degradation via reductive dechlorination or anaerobic oxidation (Wiedemeier et al. 1999). Assessing the potential for natural attenuation (NA) usually involves the following: (1) demonstration of the existence of geochemical conditions conducive to known mechanisms of chloroethene biodegradation; (2) demonstration of a distinct trend toward decreasing chloroethene concentrations; (3) demonstration of the production of daughter products indicative of chloroethene biotransformation; and (4) laboratory demonstration of an indigenous mechanism for microbial chloroethene degradation.

The third piece of this diagnostic may be complicated by volatilization of daughter products or degradation pathways with extremely short-lived or difficult to detect compounds, such as acetylene. All of these steps have been followed in the case of BDRLF though the last portion was conducted prior to the Record of Decision. As was shown in the presentation of the batch study, a microcosm study may have provided more credibility to monitored natural attenuation (MNA) for BDRLF especially combined with the evidence for natural attenuation from the site data. In the following section, I assess the potential for natural attenuation according to the USEPA protocol plus some additional considerations including phytoremediation and the BIOCHLOR model.

4.3.1 Geochemical Evidence

In the geochemical analysis conducted by BMT Entech for the RI, they state that the presence of reduced iron in all the monitoring wells except MW2 combined with the temperature and pH of the groundwater suggests favorable conditions for natural attenuation of TCE and PCE. These data are summarized in Table 19. Although, the alkalinity testing (as calcium carbonate), suggests minimal biological activity according to BMT Entech. BMT Entech asserts that biological active portions of a plume may be

identified in the field by their increased alkalinity (compared with background wells), caused by the carbon dioxide resulting from degradation of the pollutants. This statement is flawed because the addition or removal of CO_2 to a solution does not change alkalinity. Alkalinity is affected by all the processes that yield or consume H^+ or OH^- in stoichiometric equations. For example, oxygenation of soluble ferrous iron to ferric oxide decreases alkalinity by yielding 2 moles of H^+ for every mole of Fe^{2+} (Stumm and Morgan 1996).

Photosynthesis and respiration may increase or decrease alkalinity depending on the compounds involved. For example, photosynthesis will increase or decrease alkalinity depending on whether NO_3^- or NH_4^+ is used as a nitrogen source for organic matter creation because of the association of alkalinity with charge balance. Similarly, respiration processes that generate NO_3^- like aerobic bacterial decomposition of biota (nitrification) decrease alkalinity while denitrification, which degrades NO_3^- increases it. Sulfide oxidation decreases alkalinity and sulfate reduction increases it. (Stumm and Morgan 1996). Therefore the general decrease in alkalinity downgradient from the landfill may indicate active nitrification, sulfide oxidation, ferrous iron oxidation to ferric oxide and a number of other processes. These oxygen demanding processes are possible given the average DO content of 5.8 and 5.6 mg L^{-1} found in the monitoring wells and 10 geoprobe wells sampled in March 2006 and 2011 respectively. The 2011 data are shown in Table A-10.

Table 19 Geochemical data for MWs taken during RI

Sample Location	Date	pH	ORP (mvolts)	Ferrous Iron (mg L^{-1})	Alkalinity ($CaCO_3$ eq)
MW1	Jan-04	5.87	220	1.5	60
MW2	Jan-04	5.91	202	0	20
MW3	Jan-04	4.83	201	1.9	10
MW4	Jan-04	5.89	178	5.8	30
MW5	Jan-04	5.9	161	6.2	75
MW6	Jan-04	5.51	145	6.8	20
MW7	Jan-04	6.17	203	3	80
MW8	Jan-04	5.21	204	2.6	10
MW9	Jan-04	6.13	140	7.4	45

Additional geochemical data for the monitoring wells were obtained during the March 2006 groundwater sampling event. These data are presented in Figure 27 minus the chloride, nitrate, sulfate, and ethane/ethane data. Chloride was 500 mg L^{-1} for all the wells and the other parameters were not detected in any of the monitoring wells. The most striking difference between the 2004 and 2006 geochemical data is the apparent decrease in ferrous iron. However, the Fe(II), alkalinity, nitrate, sulfate, sulfide, and chloride data were all obtained using colorimetric analysis which is not a highly accurate measurement. It is unclear how the Fe(II) field measurements for the RI were taken, but the level of precision is higher suggesting a different measurement tool.

The drop in Fe(II) between the two dates corresponds to an increase in ORP which is a probable cause of the decrease in reduced iron. ORP increased from 183.3 mV to 237 mV. The average pH increased over this period from 5.7 to 6.21. Additionally, the alkalinity decreased across the site which may be linked to the oxidation of ferrous iron to ferric oxide, an alkalinity lowering process that could also help explain the decrease in Fe(II). Clearly, geochemical conditions relevant to NA are changing over time at the site. This is further exemplified by the drop in average ORP and pH to 49.0

mV and 5.8 for the 10 geoprobe wells sampled in March 2011. This illustrates the need to assess natural potential using a composite of multiple monitoring events as opposed to one or two.

The fluctuations in DO, related to the other geochemical parameters may actually favor complete degradation of chlorinated ethenes. For example, aerobic microbial degradation of DCE and VC as primary substrates has been demonstrated while the more oxidized PCE and TCE are primarily degraded under anaerobic reducing conditions (Bradley 2003). The fluctuation between the two states favors complete degradation of the chloroethene compounds. The March 2006 monitoring also showed methane production in MW4, MW7, MW8, and MW9. With consistent methane production, cometabolism of TCE by methanotrophic organisms may be occurring especially given the aerobic groundwater conditions (McCarty and Semprini 1994).

It is possible that contaminant reduction by iron monosulfide minerals such as mackinawite and pyrite is taking place at BDRLF. Iron monsosulfide minerals are formed when sulfate gets reduced to sulfide and reacts with ferrous iron (Shen and Wilson 2007). Sulfate was detected in all the wells except MW2 in March 2006, but sulfide was not detected in any of the wells. Ferrous iron concentration as high as 7.4 mg L^{-1} were found at the site and MW6 with the highest and most consistent TCE contamination had 6.8 mg L^{-1} Fe(II). MW2 was the only well to have no detectable Fe(II). Lu et al. (2008) found significant TCE degradation when in-biowall and downgradient ferrous iron concentrations never exceeded 3.25 mg L^{-1}.

He et al. (2008) found that significant degradation of TCE occurred in a biowall at incoming groundwater sulfate concentrations of 1400 to 2600 mg L^{-1} at Altus AFB. The

sulfate concentrations at BDRLF ranged from 250 to 500 mg L^{-1}. Surface and subsurbace soil iron levels are quite high ranging from 21,700 mg kg^{-1} to 6700 mg kg^{-1} and 40,400 mg kg^{-1} to 518 mg kg^{-1} respectively (Figure 16). The range of groundwater iron values was 18200 µg L^{-1} to 665000 µg L^{-1} (Table A-7). The levels of surface iron are high enough to exceed the USEPA residential soil RBC at all 20 of the RI soil boring locations. Therefore, if the groundwater conditions are reducing enough to create sulfide, then FeS would likely form and this could be a source of natural attenuation of TCE and other chlorinated solvents at the site.

Table 20 Geochemical data for MW from March 2006

Well Name	DO (mg L^{-1})	Ferrous Iron (mg L^{-1})	Alkalinity (mg L^{-1})	Temperature (°C)	pH	ORP (mvolts)	Sulfate (mg L^{-1})
MW1	3.4	0.05	40	11.95	5.37	82.6	250
MW2	8.69	0.05	0	21.04	6.52	30.1	0
MW3	5.85	0	0	11.45	6.4	19	250
MW4	8.6	0.05	0	12.07	5.49	68.3	250
MW5	7.35	0.05	40	12.57	5.35	70.6	250
MW6	6.5	0.05	0	8.29	5.61	16.6	500
MW7	4.15	0	40	10.02	6.37	19.8	250
MW8	2.92	0.05	0	8.6	5.46	54.5	250
MW9	4.67	0.05	0	11.56	5.27	94.9	250

The most important pathway for biogeochemical degradation of TCE with FeS starts with degradation to acetylene followed by fermentation to ethanol and acetate. Sulfate or iron(III) reducing bacteria then oxidize those byproducts to CO_2 (Kennedy et al. 2006). Iron reduction is known to occur at the site as evidenced by the Fe(II) found during the RI (Table A-8) so it is possible that at least the second step in this degradation pathway is occurring.

Apart from the misconstrued alkalinity data, the RI geochemical data indicates a strong likelihood of natural attenuation. BMT Entech made a similar conclusion apart from their confused interpretation of alkalinity. The March 2006 geochemical data do not generally support the occurrence of reductive dechlorination, but show the potential for cometabolism of chloroethenes and oxidation of the more reduced chloroethenes DCE and VC. Furthermore, the fluctuations in DO, ORP, and related Fe(II), and sulfate, offer the potential for complete degradation of the chloroethenes starting with PCE. It is important to note that BMT Entech concluded that the site did not favor natural attenuation after the March 2006 sampling even though the 2004 sampling strongly supported it and as a partial consequence MNA was eliminated as a favorable remedial action. When considering the potential for natural attenuation at a site it is necessary to use geochemical data from a number of time periods due to the dynamic nature of groundwater.

4.3.2 Decreasing Concentrations

PCE readily undergoes reductive dechlorination to TCE except in aerobic aquifers (Bradley 2003). Given the low occurrence of PCE found in the groundwater at the site, but high levels found during the soil gas survey, it is likely that PCE is degrading rapidly at the site. For example, MW3 was placed in its given location based on the high levels of PCE, TCE, and other chlorinated solvents at point B4 from the soil gas survey, but MW3 has never showed significant groundwater contamination. Given the high levels of degradation byproducts found at point B4 it is possible that the period of one year between soil gas surveying and groundwater sampling was enough for the groundwater contamination to completely dissipate either by biogeochemical degradation,

volatilization, plant respiration, or migration off the site. Regardless of the mechanism, there was clearly a decrease in contaminant concentration at this point. Another example of apparent PCE attenuation is seen at MW9 where PCE was detected at its highest concentrations in the soil gas survey. In January 2004 during the RI, TCE and *cis*-DCE were detected below 1 µg L^{-1} in MW9, but no contaminants were detected thereafter. It is likely that much of the contamination traveled via groundwater into the creek, but the degradation byproducts of PCE found during the RI clearly indicate that degradation was occurring.

The only well to show TCE and *cis*-DCE levels consistently elevated above trace amounts is MW2. This well has shown a steady decrease in TCE concentrations except for an aberrant spike in August 2004, probably attributable to decreased aquifer volume (Figure 19). The same spike was observed in MW6 supporting this hypothesis. On the other hand, *cis*-DCE concentrations have not significantly changed over time. This could indicate increased degradation of TCE despite decreases in its concentration. Regardless, levels of *cis*-DCE have never exceeded the 70 µg L^{-1} MCL. As seen in Figure 20, MW6 shows the same general decline in TCE concentrations as MW2 until March 2011, when concentrations spiked. This could be attributable to interception of a newer release of TCE from upgradient, as might be guessed based on the distribution of contamination in the soil gas survey (Figure 12).

As shown in Table A-6, *cis*-DCE did not appear in the well until April 2008. The next monitoring event in March 2009 showed the lowest TCE concentration to date, 0.18 µg 1,1-DCE L^{-1}, and 1.8 µg *cis*-DCE L^{-1}. In December 2010, no contamination of any kind was found, but in March 2011 concentrations spiked to 530 ug L^{-1}. The *cis*-DCE

concentration also increased to 3.4 ug L^{-1} and continued to increase in the May 2012 reading, while the TCE concentration dropped again. To understand the reason for the increase in *cis*-DCE it would be beneficial to know how the geochemistry changed over this time. As mentioned before, it may be that the increase is associated with a newer contaminant release which may for example have more dissolved electron donors to facilitate reductive dechlorination. The difficulty of interpreting MW6 data illustrates how a clearer assessment of contaminant dissipation over time would be facilitated if monitoring was conducted along transects parallel with groundwater flow.

From January 2004 to November 2005, TCE concentration in MW8 decreased. Then, they increased by a factor of 3 in September 2006 and decreased until reaching 0 in May 2012. *cis*-DCE showed a similar trend and was actually at a higher concentration in September 2006 underlining the role of reductive dechlorination. These data suggest a series of contaminant releases both of which dissipated over time.

The site data does not show unequivocal decrease in concentration for all the monitoring wells, but all wells show a general decline since monitoring began. Moreover, two wells have a pattern of decrease, spike, and decrease suggestive of multiple releases. The new releases coincide with increases of *cis*-1,2-DCE indicating conditions favorable to continued natural attenuation. The clear decreases in concentration from the soil gas survey especially for PCE and 1,1,2,2-PCA indicate that conditions at the site are reducing enough to rapidly transform the most oxidized chlorinated ethanes and ethenes.

4.3.3 Production of Daughter Products

As Entech states in the RI, the chemical evidence for reductive dechlorination at the site is clear. They reference relative concentration of PCE/TCE, and associated breakdown products in groundwater, notably wells 2, 6, and 8, but do not go into any detail. MW9 also had detectable levels of TCE and *cis*-DCE during the RI (Table A-6). The RI geoprobe sampling showed two wells (BD-B08 and BD-B15) with the complete chain of PCE reductive dechlorination byproducts, including the most reduced, VC. BD-B17 had all except VC and B10 through B12 had TCE and *cis*-DCE. Only one boring location showed a single parent compound and no reductive dechlorination degradates and this was B16 with a trace TCE concentration of 0.114 $\mu g\ L^{-1}$ (Table A-4).

Reductive dechlorination of TCE to *cis*-DCE occurs in Fe(III)-reducing conditions and in more strongly reducing environments (Chapelle 1996). The geochemical data collected during the RI shows that TCE reduction is occurring in all of the wells except MW2, which is odd considering that some of the highest *cis*-DCE levels were detected there. As shown by Bradley (2003) TCE may also be reduced under manganese (IV) reducing conditions, providing one possible explanation. Of the DCE isomers, *cis*-DCE is the most prevalent reductive dechlorination byproduct of TCE degradation. The site data supports this as *cis*-DCE was much more commonly found and detected at higher concentrations than the others. The third isomer of DCE, 1,1-DCE is primarily a transformation product of trichloroethane (TCA). This makes sense considering the high detection of TCA in the soil gas. 1,1-DCA and 1,2-DCA, more degradates of TCA, were also detected in groundwater during the SSP geoprobe sampling (Table A-3), but never at any other sampling time.

Although not considered a major natural attenuation pathway in the RI, it is possible that contaminant reduction by iron monosulfide minerals such as mackinawite and pyrite is taking place at BDRLF. Abiotic reductive dechlorination of PCE and TCE typically takes place by reductive β-elimination that results in accumulation of acetylene and other completely dechlorinated products (Dong et al. 2008). Acetylene is extremely volatile and is not likely to be found in water, making it difficult to detect in groundwater sampling for CAH degradation byproducts. Moreover, it is not considered toxic and does not appear on the USEPA Target Compound List (TCL) for VOCs.

Therefore, determining the occurrence or likelihood of natural attenuation of CAHs by FeS minerals or other reactive minerals must be achieved by analyzing soil mineralogy directly with scanning electron microscroscopy (SEM) and or x-ray diffraction (XRD) (He et al. 2008). It may be possible to indirectly judge the occurrence of FeS minerals based on soil and aqueous iron, sulfate, and redox conditions, but there is not a clear literature precedent for such judgments.

Even without data on abiotic or biogeochemical TCE and PCE degradates, we know that reductive dechlorination is occurring at the site because of the detection of lesser chlorinated ethenes since the start of monitoring in 1997. Of the monitoring wells, MW2 has showed the highest and most consistent concentration of reductive dechlorination byproducts, primarily *cis*-DCE, but MW6, MW8, and MW9 have also showed detectable levels of the DCE isomers. In addition, the three geoprobe groundwater sampling events all showed reductive dechlorination byproducts for both chlorinated ethenes and ethanes. Finally, the soil gas survey showed significant co-occurrence of parent and daughter products for both chlorinated ethenes and ethanes. In

conclusion, there appears to be significant evidence based on the daughter products detected that natural attenuation via reductive dechlorination is occurring at the site. Furthermore, the likelihood of abiotic degradation is high given the high levels of soil and aqueous iron and the reducing conditions in the groundwater.

4.3.4 Laboratory Assessment of Natural Attenuation

The batch study was not designed to solely test the ability of the site soil to naturally attenuate TCE, but a soil background sample was included to compare the biowall mixtures to the native soil. In addition, a negative control comprised solely of concrete sand was used, permitting an assessment of the remedial capacity of the site groundwater used. The soil background treatment had an average TCE degradation efficiency of 58.1%. The soil mixture used was a combination of soil boring 6 and 16 made in March 2011. Though the last replicate in the test had predominately soil boring 6 soil. This replicate showed the highest degradation efficiency, suggesting variations in the capacity of the site soil to degrade TCE. The sand spike had an average TCE degradation efficiency of 48.4%. Considering that the sand has little capacity to reduce TCE, the degradation observed must be attributable to the groundwater used. It is known from geochemical analyses conducted for the RI that the MW4 groundwater had high levels of Fe(II) relative to other sites, such as Altus Air Force Base, where lower levels of Fe(II) were associated with TCE degradation(Lu et al. 2008).

4.3.5 Phytoremediation

One source of natural attenuation not considered at BDRLF is degradation and dissipation by plant respiration. The March 2011 sampling by BMT Entech showed that groundwater at the site in the immediate vicinity of the proposed biowall is relatively shallow, with six of the 20 soil borings along the biowall footprint showing the water table at 2 feet or less. The RI states average depths to the water table range from 10 feet just north of the landfill to 1-foot or less near the southern floodplain. These statements suggest that TCE within the shallow groundwater could be respired and degraded by the trees and understory vegetation at the site as shown by Newman et al. (1999). Newman et al. showed that hybrid poplar (*Populous trichocarpa x P. deltoides)* was able to remove over 99% of the added TCE in a simulated groundwater cell 1.5 m deep. Most of the removed TCE was degraded within the plant with the remainder being transpired.

With groundwater as shallow as 0.3 meters south of the BDRLF it is possible that tree roots of tulip poplar, oak, and even understory vegetation could have actively taken up TCE laden water at BDRLF degrading and respiring it. Narayanan et al (1995) showed that alfalfa can extract TCE from groundwater via transpiration suggesting that even understory plants with much shallower root systems than a mature hardwood could contribute to the natural attenuation of TCE at the site. Anderson and Walton (1992) reported enhanced degradation TCE in the rhizosphere of a number of plants including *Lespedeza cuneata*, *Pinus taeda*, and *Glycine max.* The empirical basis for respiration of TCE by plants, degradation within the plants, and within the plant rhizosphere suggest that at heavily wooded sites with shallow groundwater natural attenuation via

phytoremediation should be considered in addition to the presence of common metabolites of biological reductive dechlorination, such as *cis*-DCE and vinyl chloride.

TCE attenuation by trees and vegetation can be tested using the solid-phase microextraction (SPME) method outlined by Sheehan et al. (2012). This technique can detect TCE and its metabolites within the trunk of a tree respiring TCE contaminated groundwater, making it a valuable tool to screen for groundwater contamination, delineate plumes, and access phytoremediation. Though, the authors note that the applicability of phytoscreening can be limited by subsurface heterogeneities, rooting depth, microbial degradation, azimuthal variations in tree contaminant concentration, infiltration of surface water, and seasonal changes in evapotranspiration.

4.3.6 BIOCHLOR Model

4.3.6.1 Initial BIOCHLOR Simulation

In the feasibility study (FS), BMT Entech used the BIOCHLOR model as a screening-level model to determine the feasibility of remediation by natural attenuation (RNA) at the BDRLF site. Here, I reevaluate the model parameters used and the results generated in addition to re-running the model using revised inputs.

Figure B-1 contains all the input data that BMT Entech used. The monitored natural attenuation (MNA) parameters needed to run the screening protocol were collected during the March 2006 round of monitoring well sampling. Data were collected for all 9 monitoring wells and included dissolved oxygen, nitrate, iron II, sulfate, sulfide, methane, ORP, pH, TOC, temperature, chloride, and target chlorinated VOCs. Using the Natural Attenuation Screening Protocol built into the model BMT Entech found a score

of "4" indicating that there is inadequate evidence for anaerobic biodegradation in the BDRLF site plume. The screening user interface is presented in Figure B-2

They then proceeded to conclude from this information alone that "the site does not appear to be a good RNA candidate" (BMT Entech 2008a). This conclusion is erroneous because it is based on a single type of natural attenuation that effects chlorinated solvents when there are a number of ways for TCE and related CAHs to degrade without human intervention. The biological means for this to occur include reductive dechloriantion, aerobic oxidation, anaerobic oxidation, and aerobic cometabolism. BIOCHLOR only addresses the potential of the first process to occur. In addition, there is the potential for phytoremediation, and biogeochemical degradation, neither of which are accounted for in the BIOCHLOR-based consideration of RNA. Because the screening protocol indicated a low chance of biotransformation, plume models were run for TCE and DCE assuming no degradation.

BMT Entech assumed a constant source concentration of 500 µg TCE L^{-1} across an 800 foot wide boundary along the southeastern and southern edge of the landfill. This assumption is not supported by the site data which shows little to no groundwater or soil contamination in most of that area except for two distinct regions with elevated TCE concentrations in groundwater and soil around MW6 and between MW2 and MW3. The former region is the only one to have reached 500 µg TCE L^{-1}. The highest documented TCE groundwater concentration in the second area is about 100 µg TCE L^{-1}. In the revised model formulation, I have represented the site with two distinct source areas each with a different plume length, source concentration, and seepage velocity. The original model assumed constant seepage velocity for the entire site which was later invalidated

by hydraulic conductivity measurements in March 2011. The change in TCE concentrations over time shown in Figure 22, Figure 23, and Figure 24 indicates that even though two source areas are assumed for the purpose of modeling chlorinated solvent transport at the site that the true source region remains unknown.

Identification of a source area or primary route of escape for TCE from the landfill would have been greatly facilitated if groundwater monitoring had been performed along transects in-line with the groundwater flow path. An example of the confusion created by the chosen groundwater monitoring approach is shown in Figure 23 wherein the highest documented TCE concentration occurs about 30 meters northeast of MW6 (RI-GW20), but then drops off to almost 0 to the northwest of this. The result is that it appears like this elevated area is a source area separate from the landfill.

Even though BMT Entech erroneously assumed a TCE source area 800 feet wide with a constant concentration of 500 µg TCE L^{-1} the model shows that after 30 years the TCE concentration would be below the MCL for TCE of 5 µg L^{-1} along the centerline of the plume at 400 feet from the origin (Figure B-4). Presumably 400 feet was chosen as the modeling distance because this is the approximate distance between the landfill boundary and unnamed creek in the southeastern direction. Running the model with the same conditions, but varying the simulation time shows that the reason for the low concentration in the biowall vicinity is that the bulk of the contamination would simply not have reached there. At 400 feet and 50 years, the TCE concentration would be 40 µg L^{-1}. At 100 years, 293 µg L^{-1} and at 200 years, 483 µg L^{-1}. This analysis assumes no source dissipation or biodegradation, which is not supported by the data, but serves as a baseline nonetheless. Discussion of the meaning of the model output outside of the

simple numerical simulation which showed low likelihood of natural attenuation is lacking in the initial interpretation.

As shown in the section on groundwater, it appears like contaminants began leaving the landfill between the mid 1940s and 1950s. To test this hypothesis using the BMT Entech simulation, field data were compared to model output generated for a 70 year simulation, the approximate amount of time between 1945 and 2011. The reference field data were taken from the March 2011 geoprobe sampling at GW07 (Figure 24) because this point is approximately 400 ft from the landfill boundary and within 10 ft of the biowall. The model output suggests a centerline concentration of 136 µg L^{-1}, which is relatively close to the field concentration of 72 µg L^{-1}. Approximately 57 years is the simulation time needed to produce the observed concentration, which would mean the assumed 500 µg TCE L^{-1} parcel crossed the landfill boundary around 1954.

The actual fate and transport of TCE at the site is more complex and not the same as represented by the BMT Entech model simulation. For example, the March 2011 sampling event (Figure 24) from which the field data was taken for comparison has enough data to estimate centerlines which can be used for a more complete comparison. Along the transect shown from GW08 to GW07 the actual values are 49, 24, and 72 µg L^{-1} for GW08, GW06, and GW07 respectively. Clearly this does not match with the biochlor model output of a constant source area gradually filling an entire transect with the source concentration.

The two point transect between MW6 and GW05, shows a concentration drop 530 µg L^{-1} to 460 µg L^{-1}. Again, this picture deviates from the initial BMT Entech site conception wherein an initial source concentration of 500 µg L^{-1} was assumed for 800 ft

around the landfill. To the southwest of GW05 by about 15 m, at GW04 the groundwater concentration was reported as 730 µg L^{-1}, suggestive that the bulk of contamination has past MW6 rather than continuing to flow through it at a fixed concentration as indicated in the model.

Altering the model simulation time and comparing output to the site data indicates that the BIOCHLOR simulation as conceived by BMT Entech does not accurately capture the complexity or general trends in TCE transport at the site. The model provided a reasonable estimate of TCE concentration for GW07 assuming TCE began leaving the landfill in the mid 1950s, but would lead the investigator to conclude 200 years would be required for the full mass of TCE to reach the creek. This is not supported by site data from March 2011 showing concentrations between 460 µg L^{-1} and 730 µg L^{-1} within 20 m of the creek. The biggest flaws in the BMT Entech model simulation were the absence of model time simulation considerations, assumed constant source area of 800 ft with a fixed concentration of 500 µg L^{-1}, and the assumption of no source dissipation or degradation.

4.3.6.2 Revised BIOCHLOR Simulation

As stated previously, two separate plumes were modeled for the revised simulation. The plumes were modeled using different source widths, flow lengths, and seepage velocities. Otherwise the input parameters were the same. The largest plume was modeled assuming a point of origin or centerline based on the location of highest TCE concentration measured in 2004 as shown in Figure 23 point RI-GW17. The concentration at this point was 758 µg L^{-1}. Using Figure 2 as a reference for groundwater flow, the distance between this point and the creek was measured to be 60 m or 197 ft.

Groundwater monitoring points within 10 meters east and west of this point had TCE concentrations below detection limits and at about 20 µg L^{-1} indicating that the plume width is less than 33 feet. Of course, the exact plume width is difficult to ascertain without further measurements, but for this application 30 feet was used. A seepage velocity of 4.3 ft yr^{-1} was used based on the hydraulic conductivities measured by BMT Entech in March 2011.

The model was initially run for 8 years because field data were available for comparison over this time frame from 2004 and 2011. The model predicts that the TCE concentration at GW07 from March 2011 would be 0 µg L^{-1}, contrary to the 72 µg L^{-1} found there. Again, the model is limited by its capacity to account for the variation in groundwater flow rates and conditions which are responsible for field concentrations. Moreover, the ability to accurately model the site is dependent on accurate source information which is also inadequate.

Regardless of the model output or manner of model formulation, the actual site data indicates the bulk of the contamination remaining at the site is found within the immediate area impacted by the planned biowall. This presents another problem which is that excavation for biowall construction will act to volatilize TCE in the area of highest measured concentration, nullifying the value of the biowall. This point is illustrated in Figure 27 which shows the biowall centerline and the approximate footprint of cleared area needed for construction indicated with the black lines 30 ft (9.15m) on either side of the centerline.

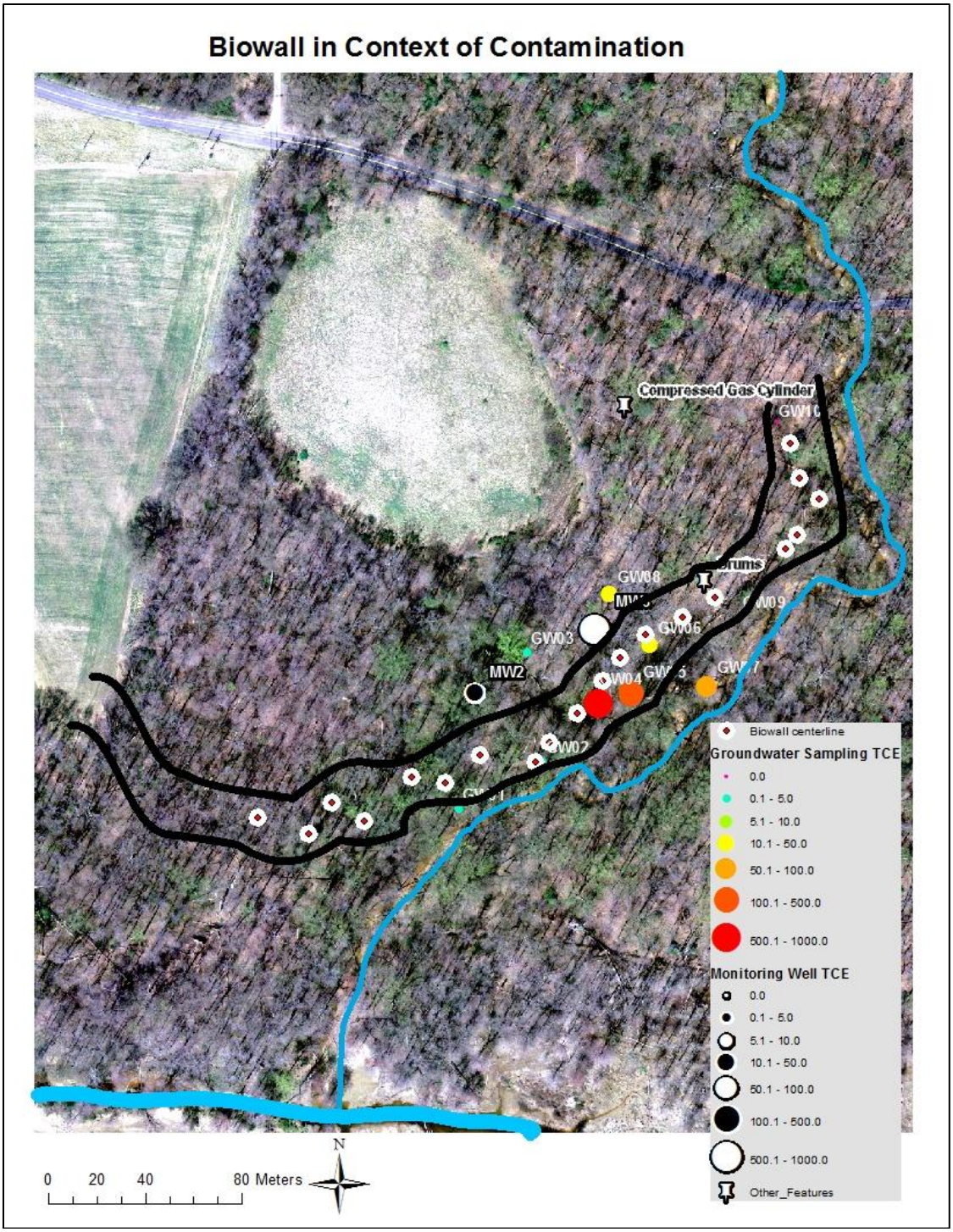

Figure 27 The biowall and its footprint in the context of site contamination detected in March 2011.

The second plume centerline and origin were based on the SSP sampling event which showed a peak concentration on the southwest corner of the landfill of 160 µg TCE L^{-1} as seen at point BA27-GW2 in Figure 22. This point is approximately 394 ft. or 120 m from the creek. To derive a plume width, Figure 22 and Figure 23 were compared and the distance between SSP-GW2 and RI-GW8 was used as the plume width based on the relatively similar concentrations found at the points of 160 µg L^{-1} and 100 µg L^{-1} TCE respectively. The distance was calculated to be 20 m or 66 ft. The seepage velocity used was 0.3 ft yr^{-1} based on the $6.88x10^{-6}$ cm s^{-1} hydraulic conductivity measured in March 2011. Figure 22 shows thatMW2 falls 50 m or 164 ft from the assumed source of SSP-GW2 along the groundwater flow path. The concentration of 57 µg TCE L^{-1} found for the SSP combined with the distance from the source can be used as an input parameter which the model automatically uses to calculate a first order reaction rate.

Assuming negligible degradation after 30 years, minimal TCE would have reached the creek or the biowall location according to the model output. Even after 100 years no TCE would make it to the creek. It would require about 500 years for any TCE to reach the biowall and this assumes no degradation which is known to occur at MW2. These model results call into question the value of placing a biowall roughly 400 feet from a mass of TCE that will not reach it for at least another 100 years and may never if natural attenuation is occurring as suggested by the batch study and the biological reductive dechlorination byproducts found in this portion of the site such as cis-1,2-DCE found in MW2 in January 1999 at 16 µg L^{-1}.

In conclusion, the revised BIOCHLOR simulation did not provide a clear picture of contaminant transport at the site and appears to be more useful as an auxiliary

analytical tool rather than the primary one. It appears that at least in the case of the first TCE source monitored on the east side of the biowall that TCE is moving faster than expected by the biowall and that the highest levels of TCE currently found at the site are within the extent of the biowall. Even without factoring the potential of biotic or abiotic degradation the BIOCHLOR model does not provide clear support for use of the biowall.

4.3.7 Contamination Dissipation

Apart from biological and abiotic degradation of chlorinated solvents at BDRLF, there is a strong possibility that the contaminants in the shallow groundwater will volatilize into to the atmosphere. This could occur from groundwater through the soil as was evident from the soil gas survey. Alternatively, volatilization can occur in the event that the groundwater intercepts the surface as would be expected in an emergent wetland. Figure 28 shows that the site contamination as of 2011 and most of the biowall extent overlap the emergent wetland boundary which includes all the area south of the dark blue line. This indicates that the possibility of groundwater interception with the ground surface is likely. MW2, where contamination and degradation have both been detected since the start of monitoring falls within this boundary. Moreover, the area south of MW6 where the majority of contamination is currently found is within this boundary.

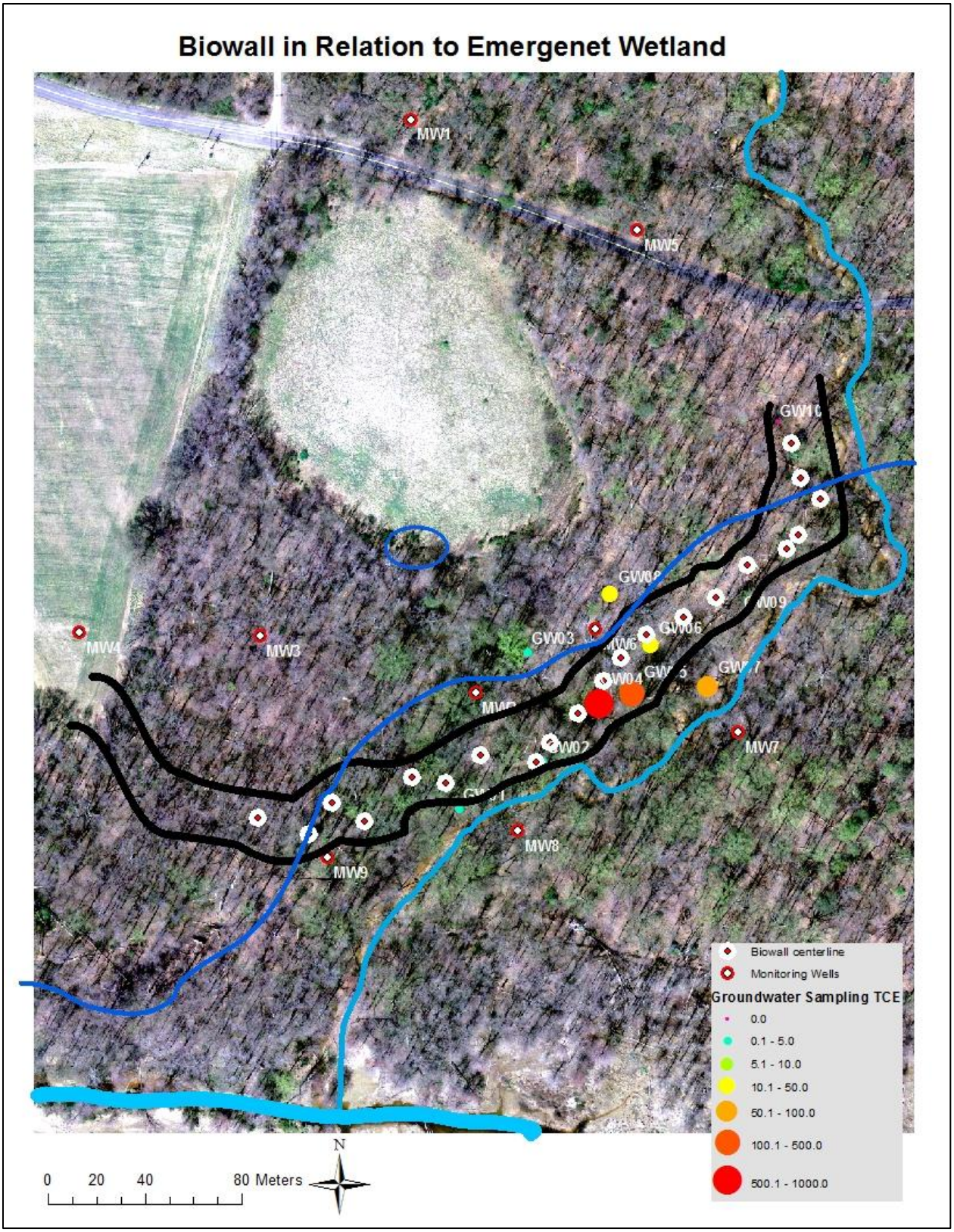

Figure 28 Biowall and site contamination in relation to the emergent wetland at BDRLF.

4.3.8 Conclusions

Application of the four-pronged USEPA approach to assessing natural attenuation showed that natural attenuation is probably occurring at BDRLF to a significant extent and that the variations observed in the reducing capacity of the groundwater may actually favor complete degradation of chlorinated ethenes. The additional phytoremediation consideration provides more support for the high likelihood of natural attenuation at BDRLF. Both BMT Entech's and the revised BIOCHLOR simulation show that the value of the simulation compared to rigorous site data analysis is limited. It was clear based on the model output that the model assumption of constant input concentrations and seepage velocities as indicated by measured hydraulic conductivities are not accurate assumptions. Finally, the consideration of TCE dissipation through volatilization and surface migration during times of site flooding provides further support for high likelihood of significant natural attenuation. Therefore, monitored natural attenuation as a remedial action for BDRLF should be reconsidered.

4.4 Assessing the Chosen Remedial Action for BDRLF

4.4.1 How will the Efficacy of the Biowall be Tested?

One post installation requirement for the biowall project will be monitoring to establish the effectiveness of the action to prevent contamination from migrating off site. To meet this end, monitoring wells would be installed along a transect perpendicular to the biowall above, within and at distances downgradient of the biowall. USDA did not establish baseline concentrations along such a transect prior to biowall installation.

Consequently it would be difficult to prove that observed differences in TCE concentrations downgradient of the biowall were caused by the biowall.

Proving the value of the biowall post-installation would also be difficult due to the limited extent of contamination at the site versus the proposed coverage of the biowall. As shown in Figure 27, only about 10% of the entire length of the proposed biowall has ever shown elevated concentrations of TCE. There is one approximately 100 foot section around and downgradient of monitoring well 6 (MW6) where BMT Entech has found concentrations of TCE at levels between 500 to 800 $\mu g\ L^{-1}$. The only other area with consistently elevated TCE concentrations is centered around MW2, but concentrations there have never exceeded 60 $\mu g\ L^{-1}$ and have generally decreased consistently albeit slowly since the first groundwater sampling in 1997.

Finally, the March 2011 monitoring event showed that the highest levels of TCE have migrated past MW6 and were at that time in the area where excavation for the biowall would occur (Figure 27). Excavating 20 feet of soil in the most contaminated area of the site would cause volatilization of the TCE defeating the purpose of the biowall. Unless it is proven that there is an indefinite source volume in the landfill, installing a 1000 foot biowall would not be warranted by the available groundwater data and it would be difficult to prove the biowall is achieving significant remediation.

4.4.2 Does the Biowall Meet the Remedial Action Objectives for the Site?

As part of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) process Remedial Action Objectives, or RAO's, are used to judge the various options considered for a site. For BDRLF, the remedial strategy chosen, the biowall, does not address the RAO's established for the site. The RAO's

were to restore the aquifer to drinking water standards within a reasonable time frame, prevent unacceptable human exposure to groundwater contamination, and to minimize future migration of groundwater contamination. Presently, the biowall is going to be placed 50 to 100 feet from the unnamed tributary to Beaverdam Creek, leaving 200 to 300 feet above gradient of the landfill before the contaminated groundwater ever contacts the biowall. In the unlikely event, that a future resident were to live at the site, the biowall would do little to improve the water quality of the aquifer for the purpose of drinking water because it is placed so close to the creek.

In other words, the first and second RAO would not be addressed due simply to the placement of the biowall. To restore the entire aquifer connected to the landfill within a reasonable time frame (RAO 1), a time frame would first have to be established. Furthermore, USDA would have to place the biowall around the landfill which is the perceived source of contamination rather than 50 to 100 ft from the unnamed creek. Then, the first RAO could be addressed assuming the biowall is capable of degrading and or sorbing the contamination assumed to be migrating from the landfill.

The biowall does not address the second RAO of preventing human exposure to the site groundwater, because again most of the area between the landfill and the creek, comprising about 500 feet, would be untreated. This RAO could be easily met by limiting long-term human exposure to the drinking water at the site. Presumably, placing the biowall closer to the landfill would do more to meet these RAO's assuming the biowall succeeds in sorbing and degrading TCE. The biowall does not minimize future migration of groundwater contamination (RAO 3) either because it addresses the

contamination once it has already entered the groundwater rather than treating it at its source.

4.4.3 Does the Biowall Address the Assessed Risk?

The risk assessment conducted as part of the remedial investigation showed that there is no significant risk to current receptors associated with exposure to surface water, sediment, or surface soil at the BDRLF. However, there was an excess lifetime cancer risk of $3x10^{-3}$, and a hazard quotient of 47 for hypothetical future adult residents, due to ingestion, dermal contact, and vapor inhalation. The excess lifetime cancer risk to hypothetical future residential children due to ingestion or dermal contact with TCE in groundwater is $1x10^{-3}$, and the hazard quotient is 102. Both of these risk factors exceed the allowable USEPA risk range of 10^{-6} to 10^{-4}.

The biowall does not address this risk because it is placed within 50 to 75 feet of the creek, leaving most of the area between the landfill and creek unaddressed. Instead the biowall as it is currently conceived would address surface water even though there is no risk associated with the surface water. This is seen with the following interpretation of the surface water data assuming roughly equal water volumes in the creek at the time of each measurement. TCE had not begun to enter the creek in 1999, but by 2004 the high concentrations around MW6 were emptying into the creek. By 2011, the initial plume had begun to dissipate as most of the TCE associated with the plume had already exited the site via the creek. In May 2012, no TCE was detected in the surface water suggesting a negligible quantity is reaching and or remaining in the creek long enough to detect.

4.4.4 Is the Perceived Risk Worth Acting On?

The only risk associated with the site is to future residents who would consume contaminated groundwater at a concentration of 435 ppb for their entire lives and to children who would do the same plus eat contaminated site soil. Even though inhabitation of this site is unlikely for many reasons including its designation as federal property, proximity to perennial streams, and wetlands, distance from desirable shopping and transportation opportunities, and limited buildable area at the site, the USDA was told to proceed with a remedial action. Then, for some reason the biowall was chosen as the remedial action for this site and placed within 100 feet of the unnamed creek doing nothing to address the only perceived risk at the site. Therefore this remedial action is flawed on two counts. It not only fails to decrease the human health risk associated with the site but is also compelled by a risk that is unlikely to ever be realized.

Finally, assuming the highly unlikely permanent inhabitation of the site downdgradient of the landfill, the number of people who would ever be exposed to the elevated levels of TCE at the site would be minimal. This is because significant contamination has only been documented in a 100 foot section at and downgradient of MW6. Monitoring since 2004 suggests that the highest levels of TCE associated with MW6 have migrated past it and will continue to enter the creek as they have since monitoring began. Such common sense considerations do not appear to be part of the standard CERCLA decision making process. Evidently, this is a shortcoming of CERCLA and may result in decisions which do not meet the USEPA mission to protect human health and the environment.

When trying to determine whether risks are worth addressing, cost benefit analysis may be employed. Unfortunately, this is not a standard tool of the CERCLA

decision making process and was therefore overlooked. Nonetheless, it seems important to weigh the impacts of this and future remedial actions on human and environmental health and to compare them to other options, being that it is USEPA's mission to protect human health and the environment. With limited potential to prove the benefits of the biowall due to its placement, low TCE concentrations at the biowall interface, the costs of this action would certainly outweigh the negligible benefits.

The costs can be broken into monetary, environmental, and social categories. For instance the proposed 1000-foot biowall would require the clearing of 2 acres of bottomland hardwood forest, special trenching machinery, an already built mixing area, a tub grinder to grind the site trees and more. These materials and actions total around $1.0 million. Environmental costs include erosion and increased sediment loads in the creek during and following construction, increased BOD in the creek, potentially decreased stream quality overall, loss of woodland habitat, soil compaction, and myriad other construction related effects.

This project will represent a significant disturbance to this site in that approximately 50 feet on either side of the biowall will have to be cleared for the passage of heavy machinery on the site. This will amount to roughly 2 acres of cleared land along the creek line. Because the creek is only 50 feet away from the proposed biowall at some points it is highly likely that the clearing activities will impact the creek. When it is unclear how the biowall will protect human health and the environment it is questionable why the USEPA favors the biowall as the remedial action for this site. These considerations show that incorporation of cost benefit analyses into the CERCLA would

increase the likelihood that remedial options with clearly established benefits would be chosen in the future.

Another problem with the assessed human health risk is that it assumes that the landfill will be a source of TCE indefinitely. This is not supported by the data, instead it appears like the TCE originally found at the site has and continues to migrate into the surface water where it is diluted and volatilized, reducing surface water concentrations to 0 by the time Beaverdam Creek is reached. This can be seen in Figure 24, which shows the highest levels of TCE (730 µg L^{-1}) approximately 75 feet downgradient of MW6. This sampling point is within the immediate flow path of the temporary well sampled in January 2004, which showed a TCE concentration of 758 µg L^{-1}. The distance between these points is again about 75 feet. With an estimated groundwater seepage velocity of 4 ft yr^{-1} and the passage of 7 years this would mean that the water at 758 µg L^{-1} could have migrated about 30 feet. Although this distance does not match the 75 feet between the two points it still suggests the migration of TCE over time.

Moreover, the calculation of seepage velocity is made based on an assumed porosity of 0.3 with little to no validation outside the assumption of homogenous silty sand aquifer material. If the porosity is changed to 0.2 then the seepage velocity would be 2.01 m yr^{-1} or 6.6 feet. With this velocity the TCE could have moved about 50 feet over 7 years assuming no retardation. Seepage velocity is also directly proportional to the hydraulic gradient which could be larger than the estimate for the rest of the site due to topographical considerations. Combine this information with the concentration of 49 µg L^{-1} found at about the same point as the 758 µg L^{-1} and it appears like the contamination around the landfill is subsiding.

On the other hand, the temporal trend in TCE concentrations for MW6 tells a slightly less clear picture regarding continued TCE release from the landfill. The highest concentrations of TCE in MW6 were found in August of 2004. The next 5 measurements up to December 2010 showed decreasing concentration in monitoring well 6 with the December 2010 reading showing no TCE. Then in March 2011, the concentrations increased back to 530 $\mu g\ L^{-1}$. This observation was explained as a continued release from the landfill, however it is not clear this is the case and spurious data could be the explanation. Meanwhile MW2 has showed a consistent though slow decrease in TCE concentration since monitoring began in 1994. The lower magnitude of change makes sense considering that groundwater flow in MW2 was found to be one order of magnitude in this well. Based on this information, it appears like the risk calculated for this site is overshadowed by the human and environmental costs of biowall construction and because risk is likely to diminish with time due to finite contaminant mass, it is not clear why the biowall is being constructed.

Chapter 5:Conclusion

The case study reevaluation called into question the assumed efficacy of biowalls by exposing a number of flaws in the interpretation of degradation data. In addition, it provided lessons and perspective usual for interpreting BDRLF site data. For example, the importance of clearly establishing transects parallel to groundwater flow for monitoring purposes which include points before, within, and downgradient of the proposed biowall location. Another useful lesson that was taken from the case study review is that the seepage velocity of groundwater must be considered when interpreting groundwater data. This concept was repeatedly applied for the reanalysis of BDRLF site data.

The site data analysis showed that the original interpretation of site data by BMT Entech was limited in scope and in some cases wrong. Moreover, data was left out of their analysis all together. Consequently, the impression of site contamination at BDRLF was oversimplified. The revised site analysis showed significant evidence of natural attenuation of site contaminants and dissipation of the contamination at the site. Finally, it showed that new releases of TCE are not occurring as was suggested by BMT Entech in March 2011.

The batch study showed that additions of zero valent iron to organic biowall media increase TCE degradation. However, in the case of BDRLF using iron additions is not economically feasible. Therefore, the unamended biowall materials would have to be used. The most favorable media on hydrologic and degradation grounds is MX1 with equal volumes of 30% mulch, 30% compost, and 60% concrete sand. MX1 showed 77.57% degradation of the total TCE mass. However, both the background soil and sand

control with site water also showed significant degradation with averages of 58.1% and 48.4%. This suggests that the site water used has some capacity to degrade TCE and that the site is favorable for natural attenuation.

Following the USEPA suggested protocol for natural attenuation assessment, showed that there is a high likelihood that natural attenuation is occurring at significant levels at the site. The original BMT Entech evaluation of natural attenuation in the RI also stated that the chemical and geological evidence for natural attenuation was strong. In the FS however, they concluded from their BIOCHLOR simulation that the site was not favorable for natural attenuation. In addition to the USEPA natural attenuation assessment process the additional considerations of phytoremediation and site-specific TCE dissipation avenues were explored. Both strongly support the significant occurrence of natural attenuation at the site.

The costs associated with construction of the biowall far outweigh the human and environmental benefits. For example, it will be difficult to prove any environmental or human benefits due to the placement of the biowall 50 to 100 feet from the unnamed creek and because clear transects parallel to groundwater flow have not been established and monitoring consistently. The risk assessed for the site is not associated with surface water and yet the biowall is placed such that this will be its primary function. Furthermore, the original risk assessed for future residents was based on invalidated assumptions about continued TCE release and inhabitation of the site.

In conclusion, the remedial action is suboptimal in that it does not protect human health and the environment as much as other possible actions, such as monitored natural attenuation. The remedial action may not have been chosen if CERCLA included cost-

benefit analyses in the remedial action decision making process. However, the biggest reason for the sub optimal remedial action at this site was that clear and testable goals were not established in the ROD and that clear flaws and shortcomings in the FS were overlooked by the USDA, USEPA, and all other parties involved. It is not known how many other remedial actions have been wrought with similar problems, but it is hoped that this thesis will help future actions meet the goal of protecting human health and the environment. To achieve this end, a number of recommendations are presented to conclude this document.

5.1 Recommendations

General

1. Include cost benefit analysis before choosing remedial actions
2. Incorporate the probability of occurrence when assessing risk
3. Develop culture of analytical thinking in USEPA so that data misrepresentation is less likely to result in poor use of taxpayer's money.
4. Account for the seasonal effects on groundwater contaminant concentrations by measuring depth to water table for volume corrections and by monitoring at least twice a year.
5. Establish transects parallel to groundwater flow along which monitoring occurs.
6. Account for more than biological reductive dechlorination when assessing MNA potential by assessing soil mineralogy, testing for CAH residues in tree tissue, and thinking about site-specific avenues for contamination dissipation such as volatilization during flooding.

Site Specific

1. Do not proceed with the biowall. Instead, continue with monitored natural attenuation.
2. Reseed the 2 acres of clear cut within 25 ft of the creek with a wildlife mix.
3. If proceeding with the biowall, use MX1 and plan to set up monitoring transects along the length of the biowall that include upgradient, within, and downgradient monitoring points.

Appendix A Site Data

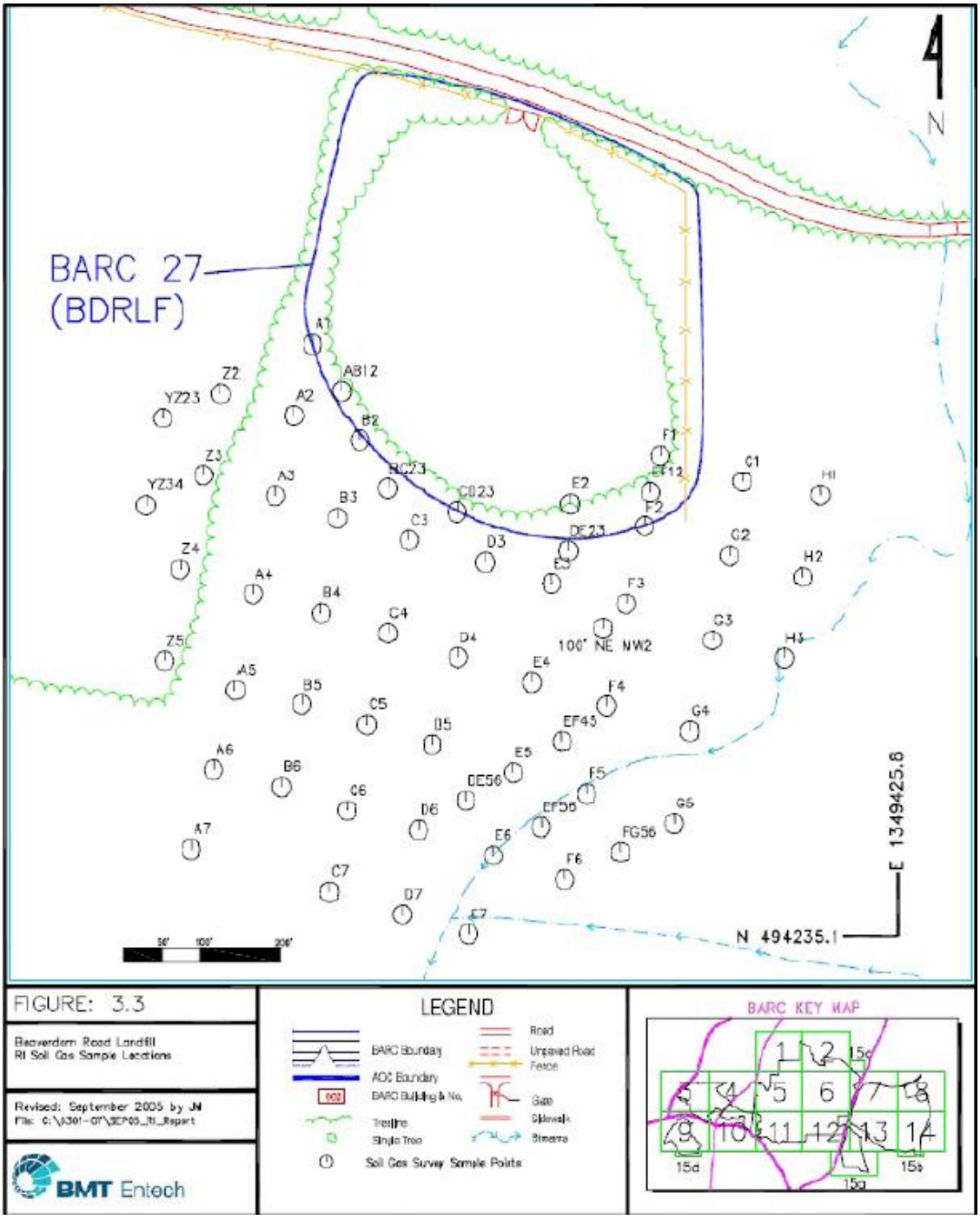

Figure A-1 Soil gas survey map.

Table A-1 Soil Gas Survey results in units of µg L^{-1}

Soil Gas Pt	Date	PCE	TCE	*cis*-1,2-DCE	*trans*-1,2 DCE	1,1-DCE	1,1,2,2-PCA	1,1,1-TCA	1,1-DCA	1,2-DCP
B4	Nov-02	71.44	75.56	59.3	19.01	36.68	57.02	41.98	46.32	99.05
G2	Nov-02	33.11	64.74	18.39	5.09	5.48	71.82	9.8	10.68	71.82
A4	Nov-02	15.39	19.52	3	1.3	0	119.76	2.12	1.87	13.92
EF12	Nov-02	0	16.12	0	0	0	0	0	0	0
E3	Nov-02	0	11	0	0	0	0	0	0	0
A3	Nov-02	4.96	8.73	0	0	0	297.94	0	0	0
EF45	Nov-02	1054.68	4.1	0	0	0	0	0	0	0
Z3	Nov-02	2.21	2.12	0	0	0	3.61	0	0	0
A1	Nov-02	0	0	0	0	0	1.58	0	0	0
A2	Nov-02	0	0	0	0	0	0	0	0	0
A5	Nov-02	0	0	0	0	0	0	0	0	0
A6	Nov-02	0	0	0	0	0	0	0	0	0
A7	Nov-02	0	0	0	0	0	0	0	0	0
AB12	Nov-02	25.75	0	0	0	0	0	0	0	0
B2	Nov-02	0	0	0	0	0	0	0	0	0
B3	Nov-02	0	0	0	0	0	0	0	0	0
B5	Nov-02	0	0	0	0	0	0	0	0	0
B6	Nov-02	0	0	0	0	0	0	0	0	0
BC23	Nov-02	6.34	0	0	0	0	0	0	0	0
C3	Nov-02	0	0	0	0	0	0	0	0	0
C4	Nov-02	0	0	0	0	0	0	0	0	0
C5	Nov-02	0	0	0	0	0	0	0	0	0
C6	Nov-02	0	0	0	0	0	0	0	0	0
C7	Nov-02	0	0	0	0	0	1.43	0	0	0
CD23	Nov-02	3.05	0	0	0	0	0	0	0	0
D3	Nov-02	0	0	0	0	0	0	0	0	0
D4	Nov-02	0	0	0	0	0	0	0	0	0
D5	Nov-02	0	0	0	0	0	0	0	0	0
D6	Nov-02	0	0	0	0	0	2.16	0	0	0
D7	Nov-02	0	0	0	0	0	0	0	0	0
DE56	Nov-02	432.02	0	0	0	0	0	0	0	0
E2	Nov-02	0	0	0	0	0	0	0	0	0
E4	Nov-02	0	0	0	0	0	0	0	0	0
E5	Nov-02	0	0	0	0	0	1.3	0	0	0
E6	Nov-02	75.29	0	0	0	0	0	0	0	0
E7	Nov-02	0	0	0	0	0	0	0	0	0
EF56	Nov-02	85.73	0	0	0	0	0	0	0	0
F1	Nov-02	0	0	0	0	0	0	0	0	0
F2	Nov-02	260.39	0	0	1.63	0	0	0	0	0
F3	Nov-02	0	0	0	0	0	0	0	0	0

F4	Nov-02	0	0	0	0	0	0	0	0	0
F5	Nov-02	0	0	0	0	0	0	0	0	0
F6	Nov-02	0	0	0	0	0	0	0	0	0
FG56	Nov-02	0	0	0	0	0	0	0	0	0
G1	Nov-02	0	0	0	0	0	0	0	0	0
G3	Nov-02	0	0	0	0	0	0	0	0	0
G4	Nov-02	0	0	0	0	0	0	0	0	0
G5	Nov-02	0	0	0	0	0	0	0	0	0
H1	Nov-02	0	0	0	0	0	0	0	0	0
H2	Nov-02	0	0	0	0	0	0	0	0	0
H3	Nov-02	0	0	0	0	0	0	0	0	0
YZ23	Nov-02	0	0	0	0	0	0	0	0	0
YZ34	Nov-02	0	0	0	0	0	0	0	0	0
Z2	Nov-02	0	0	0	0	0	0	0	0	0
Z4	Nov-02	0	0	0	0	0	0	0	0	0
Z5	Nov-02	0	0	0	0	0	0	0	0	0

Table A-2 Soil iron at BDRLF

Well Name	Date	Total Surface Iron (mg kg^{-1})	Total Subsurface Iron (mg kg^{-1})
BD-B01	Jan-04	19200	1380
BD-B02	Jan-04	15900	3500
BD-B03	Jan-04	20100	3340
BD-B04	Jan-04	17800	742
BD-B05	Jan-04	10900	5330
BD-B06	Jan-04	8870	2070
BD-B07	Jan-04	7490	34200
BD-B08	Jan-04	7490	13700
BD-B09	Jan-04	14500	15800
BD-B10	Jan-04	10500	8120
BD-B11	Jan-04	9040	40400
BD-B12	Jan-04	14100	8590
BD-B13	Jan-04	16400	1770
BD-B14	Jan-04	21700	18700
BD-B15	Jan-04	18600	561
BD-B16	Jan-04	13100	20700
BD-B17	Jan-04	7790	518
BD-B18	Jan-04	11400	1380
BD-B19	Jan-04	8930	744
BD-B20	Jan-04	6700	6700

Table A-3 1999 SSP geoprobe groundwater sampling results in µg L^{-1}

Well Name	Date	PCE	TCE	*cis*-1,2-DCE	1,1-DCE	VC	1,1-DCA	1,2-DCA
BA27-GW1	Jan-99	0.00	0.00	0.00	0.00	0.00	0.00	0.00
BA27-GW2	Jan-99	0.00	160.00	0.00	0.00	0.00	0.00	0.00
BA27-GW3	Jan-99	0.00	0.31	0.00	0.00	0.00	0.00	0.33
BA27-GW4	Jan-99	0.28	810.00	0.00	0.00	0.00	0.00	0.00
BA27-GW5	Jan-99	0.00	0.00	0.00	0.00	0.00	0.00	0.69
BA27-GW6	Jan-99	0.00	0.72	0.00	0.00	0.00	0.00	0.00
BA27-GW7	Jan-99	0.00	0.83	0.00	0.00	0.36	0.00	0.00
BA27-GW8	Jan-99	0.00	4.50	0.00	0.00	0.00	1.00	0.00
BA27-GW9	Jan-99	0.00	0.18	0.00	0.00	0.00	1.10	0.00

Table A-4 2004 RI geoprobe groundwater sampling results in µg L^{-1}

Well Name	Date	PCE	TCE	1,1-DCE	*cis*-1,2-DCE	*trans*-1,2-DCE	VC
BD-B01	Jan-04	0	0	0	0	0	0
BD-B02	Jan-04	0	0	0	0	0	0
BD-B03	Jan-04	0	0	0	0	0	0
BD-B04	Jan-04	0	0	0	0	0	0
BD-B05	Jan-04	0	0	0	0	0	0
BD-B06	Jan-04	0	0	0	0	0	0
BD-B07	Jan-04	0	0.609	0	0	0	0
BD-B08	Jan-04	0.14	92.6	0.36	3.47	0.643	0.14
BD-B09	Jan-04	0	0	0	0	0	0
BD-B10	Jan-04	0	30.4	0	0.444	0	0
BD-B11	Jan-04	0	11.8	0	0.15	0	0
BD-B12	Jan-04	0	2.28	0	0.524	0	0
BD-B13	Jan-04	0	0	0	0	0	0
BD-B14	Jan-04	0	0	0	0	0	0
BD-B15	Jan-04	0.218	21.4	0.176	3.38	0.341	0.347
BD-B16	Jan-04	0	0.114	0	0	0	0
BD-B17	Jan-04	0.231	758	0.445	1.52	0.261	0
BD-B18	Jan-04	0.145	396	0.228	0	0	0
BD-B19	Jan-04	0	0	0	0	0	0
BD-B20	Jan-04	0	16.0	0	0	0	0

Table A-5 2011 geoprobe sampling results in μg L^{-1}

Well Name	Date	PCE	TCE	1,1-DCE	*cis*-1,2-DCE	*trans*-1,2-DCE	VC
GW01	Mar-11	0	1.5	0	0.37	0	0
GW02	Mar-11	0	1.8	0	0	0	0
GW03	Mar-11	0	2	0	0	0	0
GW04	Mar-11	0	730	0	2.1	0.22	0
GW05	Mar-11	0	460	1	8	0	0
GW06	Mar-11	0	24	0	0.25	0	0
GW07	Mar-11	0	72	0	1.3	0	0
GW08	Mar-11	0	49	0	0.29	0	0.36
GW09	Mar-11	0	0	0	0	0	0
GW10	Mar-11	0	0	0	0	0	0

Table A-6 Monitoring well data in µg L^{-1}

a. Monitoring Well 1

Date	TCE	1,1-DCE	*cis*-1,2-DCE
Jun-97	0	0	0
Jan-99	45	0	0
Jan-04	0	0	0
Aug-04	0	0	0
Feb-05	0	0	0
Nov-05	0	0	0
Sep-06	0	0	0
Apr-08	0	0	0
Mar-09	0	0	0
Dec-10	0	0	0
May-12	0	0	0

b. Monitoring Well 2

Date	TCE	1,1-DCE	*cis*-1,2-DCE	*trans*-1,2-DCE
Jun-97	64	0	12	0
Jan-99	66	0	16	0
Jan-04	57	0	11	0.964
Aug-04	75	0	19	0
Feb-05	59	0	17	0
Nov-05	46	0	14	0
Sep-06	46	0	14	0
Apr-08	42	0	6	0
Mar-09	43	0	8.8	0
Dec-10	39	0	9	0
Mar-11	41	0	10	0
May-12	42	0	12	0

d. Monitoring Well 4

Date	TCE	1,1-DCE	cis-1,2-DCE
Jun-97	0	0	0
Jan-99	0	0	0
Jan-04	0	0	0
Aug-04	0	0	0
Feb-05	0	0	0
Nov-05	0	0	0
Sep-06	0	0	0
Apr-08	0	0	0
Mar-09	0	0	0
Dec-10	0	0	0
May-12	0	0	0

c. Monitoring Well 3

Date	TCE	1,1-DCE	*cis*-1,2-DCE	1,2-DCA
Jun-97	0	0	0	0
Jan-99	0	0	0	1.6
Jan-04	0	0	0	0
Aug-04	0	0	0	0
Feb-05	0	0	0	0
Nov-05	0	0	0	0
Sep-06	0	0	0	0
Apr-08	0	0	0	0
Mar-09	0	0	0	0
Dec-10	0	0	0	0
May-12	0	0	0	0

e. Monitoring Well 5

Date	TCE	1,1-DCE	*cis*-1,2-DCE
Jan-04	0	0	0
Aug-04	0	0	0
Feb-05	0	0	0
Nov-05	0	0	0
Sep-06	0	0	0
Apr-08	0	0	0
Mar-09	0	0	0
Dec-10	0	0	0
May-12	0	0	0

f. Monitoring Well 6

Date	PCE	TCE	1,1-DCE	cis-1,2-DCE
Jan-04	0.143	435	0.97	0
Aug-04	0	610	0	0
Feb-05	0	475	0	0
Nov-05	0	275	0	0
Sep-06	0	420	0	0
Apr-08	0	320	0	2
Mar-09	0	130	0.18	1.8
Dec-10	0	0	0	0
Mar-11	0	530	0	3.4
May-12	0	430	0.53	8.6

g. Monitoring Well 7

Date	TCE	1,1-DCE	*cis*-1,2-DCE
Jan-04	0	0	0
Aug-04	0	0	0
Feb-05	0	0	0
Nov-05	0	0	0
Sep-06	0	0	0
Apr-08	0	0	0
Mar-09	0	0	0
Dec-10	0	0	0
May-12	0	0	0

h. Monitoring Well 8

Date	TCE	1,1-DCE	*cis*-1,2-DCE
Jan-04	0.573	0	0.505
Aug-04	0.275	0	0.19
Feb-05	0.25	0	0.2
Nov-05	0.2	0	0.19
Sep-06	0.635	0	0.875
Apr-08	0.61	0	0.53
Mar-09	0.37	0	0.3
Dec-10	0.18	0	0.18
May-12	0	0	0

i. Monitoring Well 9

Date	TCE	1,1-DCE	*cis*-1,2-DCE
Jan-04	0.605	0	0.539
Aug-04	0	0	0
Feb-05	0	0	0
Nov-05	0	0	0
Sep-06	0	0	0
Apr-08	0	0	0
Mar-09	0	0	0
Dec-10	0	0	0
May-12	0	0	0

Table A-7 Total iron measured during the RI in 20 temporary geoprobe wells

Well Name	Date	Iron ($\mu g\ L^{-1}$)
BD-B01	Jan-04	45100
BD-B02	Jan-04	147000
BD-B03	Jan-04	665000
BD-B04	Jan-04	113000
BD-B05	Jan-04	102000
BD-B06	Jan-04	466000
BD-B07	Jan-04	252000
BD-B08	Jan-04	111035
BD-B09	Jan-04	335000
BD-B10	Jan-04	18200
BD-B11	Jan-04	27700
BD-B12	Jan-04	202000
BD-B13	Jan-04	245000
BD-B14	Jan-04	103000
BD-B15	Jan-04	112000
BD-B16	Jan-04	143000
BD-B17	Jan-04	36600
BD-B18	Jan-04	23000
BD-B19	Jan-04	74900
BD-B20	Jan-04	276000

Table A-8 Iron data for monitoring wells sampled during RI

Sample Location	Total ($\mu g\ L^{-1}$)	Dissolved ($\mu g\ L^{-1}$)	Fe(II) ($mg\ L^{-1}$)
MW1	4300	1130	1.5
MW2	4350	0	0
MW3	3780	1750	1.9
MW4	9000	7740	5.88
MW5	8260	7910	6.2
MW6	16200	13600	6.8
MW7	3840	3170	3
MW8	6670	3510	2.6
MW9	22100	19700	7.4

Table A-9 Iron data for monitoring wells sampled for the baseline groundwater sampling in 1997

Sample Location	Total ($\mu g\ L^{-1}$)	Dissolved ($\mu g\ L^{-1}$)
MW1	2530	1180
MW2	5460	3410
MW3	4300	430
MW4	14200	12200

Table A-10 Geochemical parameters from March 2011 geoprobe sampling

Well Name	Depth (ft)	Date-time	DO ($mg\ L^{-1}$)	Temperature (°C)	pH	ORP (mvolts)	Turbidity (NTU)
GW01	9	3/18/11 10:30	3.4	11.95	5.37	82.6	>999
GW02	6 to 10	3/18/2011	8.69	21.04	6.52	30.1	>999
GW03	16	3/15/2011 13:00	5.85	11.45	6.4	19	>999
GW04	12	3/17/11 14:48	8.6	12.07	5.49	68.3	242.9
GW05	8 to 12	3/17/2011 1:56	7.35	12.57	5.35	70.6	70.5
GW06	12	3/17/2011 9:05	6.5	8.29	5.61	16.6	>999
GW07	8 to 12	3/17/2011 9:57	4.15	10.02	6.37	19.8	488.7
GW08	10	3/15/2011 11:59	2.92	8.6	5.46	54.5	>999
GW09	8 to 12	3/17/2011 11:50	4.67	11.56	5.27	94.9	>999
GW10	12	3/18/2011 11:40	3.36	14.58	5.91	33.2	9.1

Appendix B BIOCHLOR Simulation

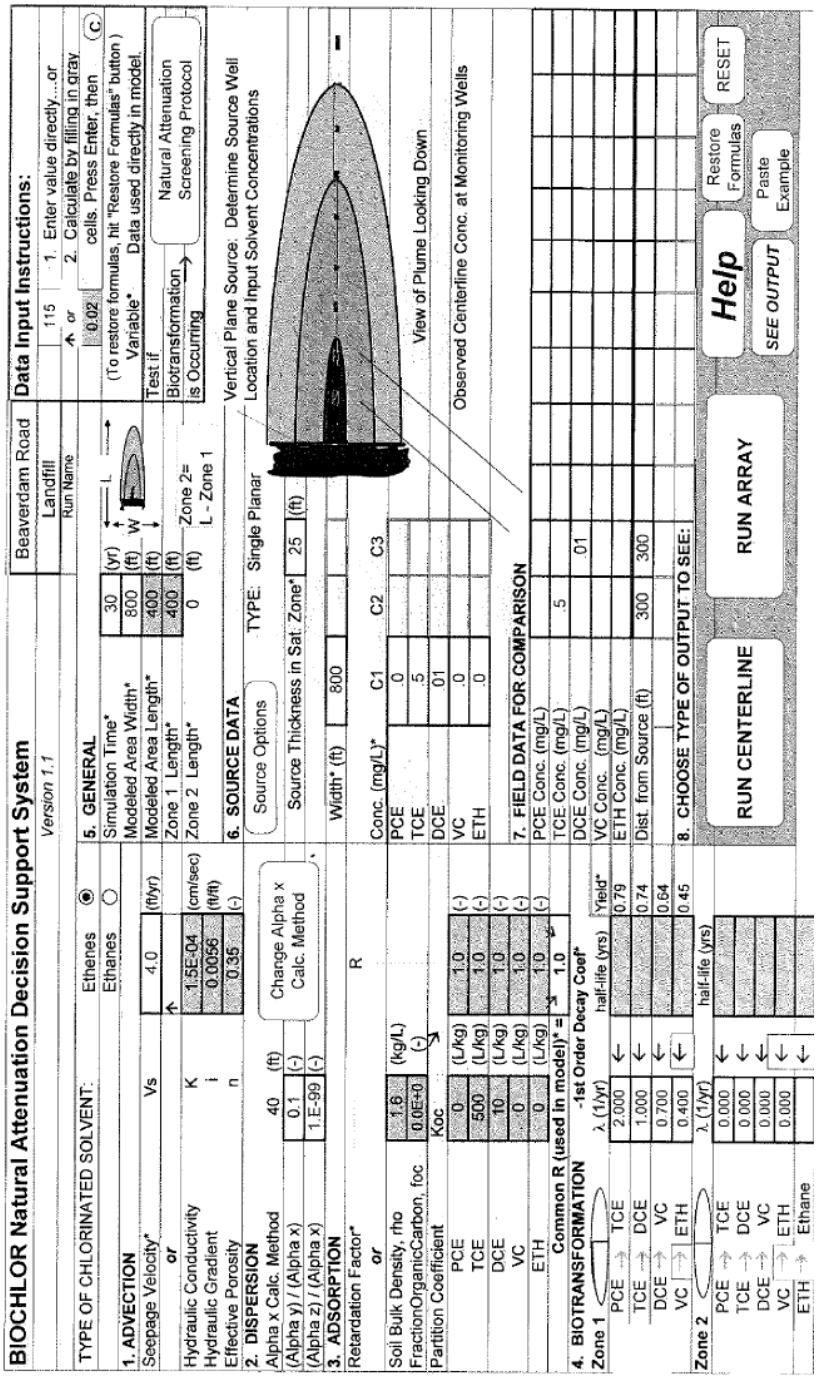

Figure B-1 BIOCHLOR input interface showing parameters used by BMT Entech

Natural Attenuation Screening Protocol

Interpretation	Score
Inadequate evidence for anaerobic biodegradation* of chlorinated organics	0 to 5
Limited evidence for anaerobic biodegradation* of chlorinated organics	6 to 14
Adequate evidence for anaerobic biodegradation* of chlorinated organics	15 to 20
Strong evidence for anaerobic biodegradation* of chlorinated organics	>20

Score: 4

Scroll to End of Table

Analysis	Concentration in Well Contam Zone	Interpretation	Yes	No	Points Awarded
Oxygen*	<0.5 mg/L	Tolerated, suppresses the reductive pathway at higher concentrations	○	●	0
	>5mg/L	Not tolerated, however, VC may be oxidized aerobically	●	○	-3
Nitrate*	<1 mg/L	At higher concentrations may compete with reductive pathway	●	○	2
Iron II*	>1 mg/L	Reductive pathway possible; VC may be oxidized under Fe(III)-reducing conditions	○	●	0
Sulfate*	<20 mg/L	At higher concentrations may compete with reductive pathway	○	●	0
Sulfide*	>1 mg/L	Reductive pathway possible	○	●	0
Methane*	>0.5 mg/L	VC oxidized	●	○	0
	>0.5 mg/L	Ultimate reductive daughter product. VC Accumulates	●	○	3
Oxidation Reduction Potential* (ORP)	<50 millivolts (mV)	Reductive pathway possible	○	●	0
	<-100mV	Reductive pathway likely	○	●	0
pH*	5 < pH < 9	Optimal range for reductive pathway	●	○	0
	5 > pH >9	Outside optimal range for reductive pathway	○	●	0
TOC	>20 mg/L	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	○	○	0
Temperature*	>20°C	At T >20°C biochemical process is accelerated	○	●	0
Carbon Dioxide	>2x background	Ultimate oxidative daughter product	○	○	0
Alkalinity	>2x background	Results from interaction of carbon dioxide with aquifer minerals	○	●	0
Chloride*	>2x background	Daughter product of organic chlorine	○	●	0
Hydrogen	>1 nM	Reductive pathway possible; VC may accumulate	○	◇	0
	<1 nM	VC oxidized	○	○	0
Volatile Fatty Acids	>0.1 mg/L	Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source	○	○	0
BTEX*	>0.1 mg/L	Carbon and energy source; drives dechlorination	○	●	0
PCE*		Material released	○	●	0
TCE*		Material released	●	○	0
		Daughter product of PCE *	○	●	0
DCE*		Material released	○	●	0
		Daughter product of TCE If cis is greater than 86% of total DCE it is likely a daughter product of TCE*; 1,1-DCE can be a chem. reaction product of TCA	●	○	3
VC*		Material released	○	●	0
		Daughter product of DCE*	○	●	0
1,1,1-Trichloroethane*		Material released	○	●	0
DCA		Daughter product of TCA under reducing conditions	○	●	0
Carbon Tetrachloride		Material released	○	●	0
Chloroethane*		Daughter product of DCA or VC under reducing conditions	○	●	0
Ethene/Ethane	>0.01 mg/L	Daughter product of VC/ethene	○	●	0
	>0.1 mg/L	Daughter product of VC/ethene	○	●	0
Chloroform		Material released	○	●	0
		Daughter product of Carbon Tetrachloride	○	●	0
Dichloromethane		Material released	○	●	0
		Daughter product of Chloroform	○	●	0

* required analysis

+/- Points awarded only if it can be shown that the compound is a daughter product (i.e., not a component of the source NAPL)

SCORE

Reset

Figure B-2 RNA screening interface.

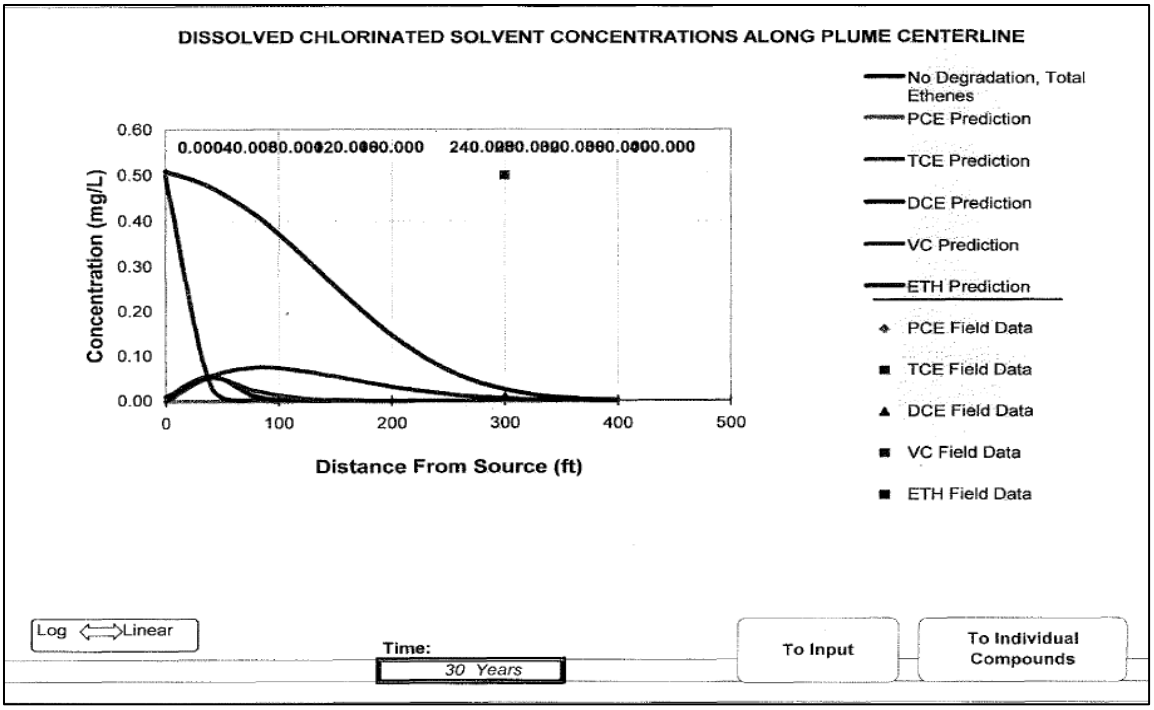

Figure B-3 Graph of dissolved chlorinated solvent concentrations along plume centerline

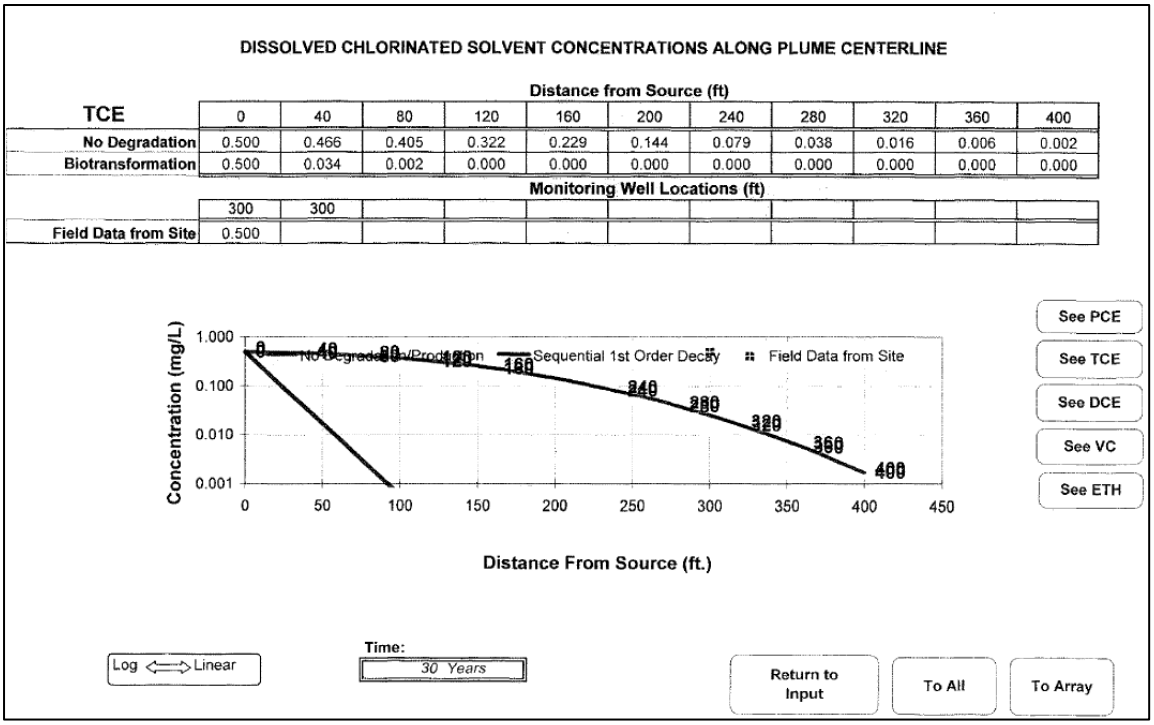

Figure B-4 Table and graph showing TCE concentrations along the plume centerline

Appendix C Temperature Data

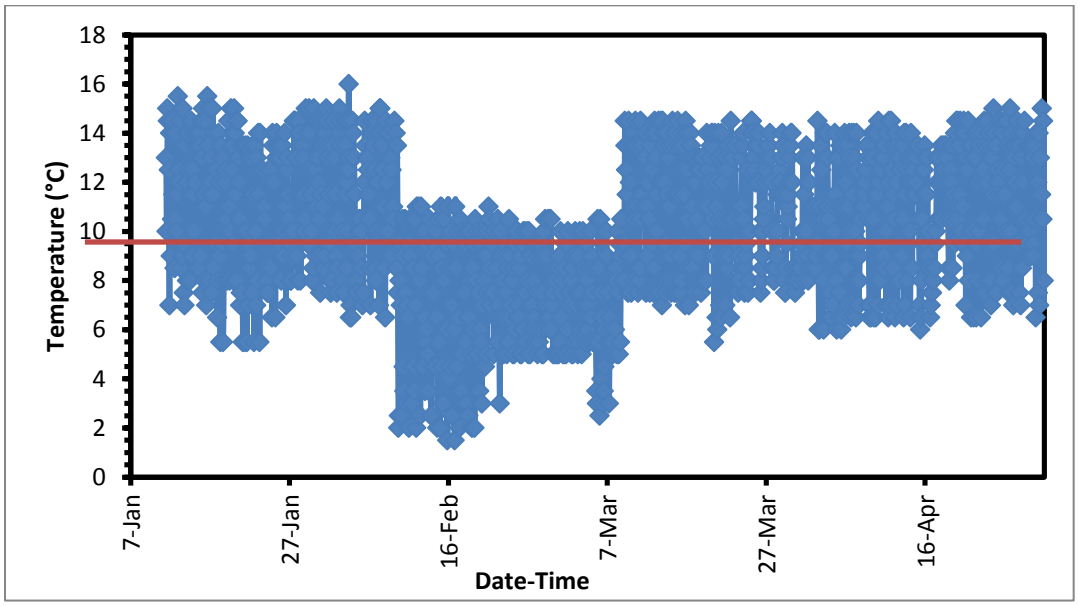

Figure C-1 Temperature change over time in cooler 1. Red line indicates mean of 10.2 °C.

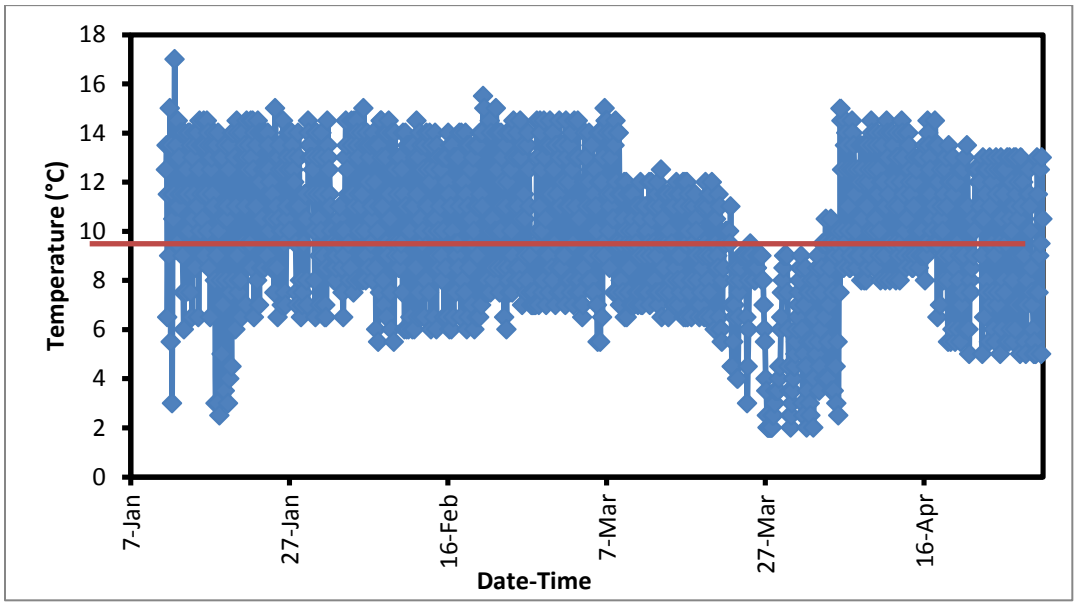

Figure C-2 Temperature profile over time for cooler 2. The red line indicates a mean of 10.04 °C.

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